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THE

PHYSICAL REVIEW.

THEORY OF LONGITUDINAL VIBRATIONS OF VISCOUS RODS.

By W. G. Cady.

Synopsis.

Theory of Longitudinal Vibrations of Thin Rods, Taking into Account Damping.—Starting with the general differential equation of wave-motion in one dimension including a viscosity term, expressions are derived for the wave-velocity and logarithmic decrement in the case of *free vibrations* of the rod. The velocity is practically the same as for undamped vibrations, while the decrement is proportional to the viscosity and to the frequency. The equation is also solved for the case of *forced vibrations due to two simple harmonic forces at the ends*, equal in amplitude but opposite in phase. If the damping is small and frequency, $\omega/2\pi$, is near the resonance frequency, $\omega_0/2\pi$, the expression for the displacement of the end of the rod is very simple: $\xi = (4X_0 l/\pi G\delta) \cos\theta \sin(\omega t - \theta)$, where $\tan\theta = -2\pi(\omega_0 - \omega)/\omega_0\delta$, δ is the logarithmic decrement per period, l the length of the rod, X_0 the maximum value of the periodic stress, and G Young's modulus. It is shown that this expression may also be obtained by reducing the rod to an equivalent system possessing one degree of freedom.

§ 1. *General Equations of Wave-Motion in Rods.*—Our starting point is the following equation, which is exactly analogous to that for plane waves in an extended medium:[1]

$$\frac{\partial^2\xi}{\partial t^2} = P\frac{\partial^2\xi}{\partial x^2} + Q\frac{\partial^3\xi}{\partial x^2\partial t}. \tag{1}$$

ξ is the displacement, at the time t, of that cross-section of the rod whose undisturbed coördinate is x. P is defined by the equation $P = G/\rho$, where G is Young's modulus and ρ the density. P is therefore the square of the wave-velocity in the absence of damping. As long as lateral effects can be ignored, it does not matter whether the material is isotropic or not: G is in any case the modulus along the axis of the rod. For brevity, we call Q the "viscosity," and treat it as a constant of the material, implying thereby that it is independent of the frequency. Its

[1] See, for example, Lamb's Dynamical Theory of Sound, 1910, Chap. VI.; or Lamb's "Hydrodynamics," 1916, Chap. XI.

possible dependence upon frequency can be tested by experiment. We shall leave aside all consideration of the mechanism by which the energy is dissipated in the material, and assume nothing further than that the frictional force is proportional to the rate of deformation. The dimensions of Q are $[L^2T^{-1}]$.

Since in this paragraph we are concerned only with damped sine-waves of any length, we may write the solution of (1) thus:

$$\xi = A\epsilon^{-jkx-bt}, \tag{2}$$

where

$$b = \eta + j\omega \tag{2a}$$

and A is a quantity dependent upon boundary conditions. k is the wave-length constant, η the attenuation-constant (that is, attenuation with time: attenuation in space need not be considered). $\omega = 2\pi f$ is the frequency-constant, or angular velocity.

On substituting (2) and (2a) in (1), and equating real and imaginary parts, we derive the following relations. For the attenuation-constant, we find

$$\eta = \frac{Qk^2}{2}. \tag{3}$$

The wave-velocity is

$$c = \frac{\omega}{k} = \pm\sqrt{P - \frac{Q^2k^2}{4}}. \tag{4}$$

On substituting this value in (2), we find for the displacement at any point

$$\xi = A\epsilon^{-Q^2k^2t/2}\cos(kx \pm \omega t). \tag{5}$$

From (4) and (5) it follows that

$$k = \frac{2\pi}{\lambda}, \tag{6}$$

where $\lambda = c/f$ represents the wave-length.

From (3), (5), and (6), the logarithmic decrement per period is found to be

$$\delta = \frac{\eta}{f} = \frac{Qk^2}{2f} = \frac{\pi\omega Q}{c^2}. \tag{7}$$

In order that a system of stationary waves may exist, the length l of the rod must be equal to an integral number of half wave-lengths. If this number is even, the center of the rod must also be free. Hence the wave-length constant for the fundamental or any harmonic is, by eq. (6), $k = \pi m/l$, in which m is any positive integer. The value for $m = 1$

gives the fundamental. From (4) and (7) it is evident that the damping increases, while the wave-velocity decreases, with increasing order of harmonics. For all practical purposes the change in velocity may be neglected; hence (always ignoring lateral effects) to a very close degree of approximation the harmonics have frequencies 2, 3, 4 $\cdots$ times the fundamental frequency.

§ 2. *Forced Vibrations.*—We will first solve the problem for the motion of a rod whose center is fixed, and at whose opposite ends two longitudinal simple-harmonic forces of like amplitude but opposing phases are applied; for the present paper originated in connection with a study of high-frequency vibrations of piezo-electric crystals and mathematically, the problem stated is identical with the problem of piezo-electric excitation, in which an impressed alternating electric field produces an alternating longitudinal mechanical stress, which at any instant is uniform throughout the rod, and numerically equal to the fictitious stress at either end. The identity of the two problems follows from the fact that the terminal conditions are the same, being expressed by eq. (11) below.

Assuming throughout that a steady state of vibration has been reached, so that the decrement η/f is compensated by an equal and opposite *increment*, we write the solution of (1) in the form

$$\xi = A\epsilon^{-j\omega t}, \tag{8}$$

in which A is a complex function of x, involving both the amplitude of ξ and the phase-difference between ξ and the impressed forces.

After the usual differentiations and substitutions, we find

$$\frac{\partial^2 A}{\partial x^2} = \gamma^2 A, \tag{9}$$

in which

$$\gamma^2 = \frac{\omega^2}{-P + j\omega Q}. \tag{10}$$

We take the origin at the center of the rod, so that the latter extends from $-l/2$ to $+l/2$. Let the impressed periodic stress at the ends of the rod have the form $X = X_0 \cos \omega t$, or, in exponential form, $X = X_0\epsilon^{-j\omega t}$ (dynes per cm.^{2}). Then at the end, where $x = l/2$,

$$G\frac{\partial \xi}{\partial x} = X_0\epsilon^{-j\omega t}, \tag{11}$$

where G is Young's modulus as before.

Equation (9) is now integrated, the constants being determined from (11) and the fact that, when $x = 0$, $\xi = 0$ and $A = 0$. In order to

save space, we omit the steps of the solution, which is most conveniently expressed in the form[1]

$$A = \frac{X_0}{G\gamma} \cdot \frac{\sinh \gamma x}{\cosh \frac{\gamma l}{2}} \cdot \tag{12}$$

Since, by eq. (10), γ is a function of the fundamental constants, it is evident that from (12) the amplitude and phase of the motion at any point along the rod can be derived.

From here on we shall be concerned only with the motion at the ends of the rod. The value assumed at the ends by A, which we will call A_0, is obtained by setting $x = l/2$ in eq. (12):

$$A_0 = \frac{X_0}{G\gamma} \tanh \frac{\gamma l}{2} \cdot \tag{13}$$

§ 3. In order to apply the last equation to actual cases, and in particular to use it for the determination of Q, it is necessary to reduce it to a more workable form. Upon reduction of (10), having regard to (3), (4), and (6), we find that, as long as Q is small,

$$\gamma = -\frac{\eta}{c} + jk = \frac{1}{c}(-\eta + j\omega). \tag{14}$$

This equation holds to a high degree of precision, even if the logarithmic decrement is as large as 0.1.

On substituting this value of γ in (13), and making obvious reductions and approximations, we arrive at the following expression for A_0, which is very accurate as long as Q is small enough to be ignored in (4) and n is small in comparison with ω:

$$A_0 = \frac{X_0}{Gk} \cdot \frac{4}{\frac{4\pi^2 n^2}{\omega_0^2} + \delta^2} \left(\frac{2\pi n}{\omega_0} + j\delta \right) = k_1 + jk_2, \tag{15}$$

in which the real coefficients k_1 and k_2 are written for brevity. ω_0 is the angular velocity at resonance (see footnote under § 4), and n denotes the difference $\omega_0 - \omega$, $\omega/2\pi$ being any frequency not far from resonance; n may therefore be regarded as a measure of the *dissonance* corresponding to any frequency.

From (15), together with (8), we readily find for the displacement at the end of the rod at any time t,

[1] In the abstract of this paper which appeared in the PHYSICAL REVIEW, Vol. 15, p. 146, 1920, the factor $\sinh \gamma x$ was erroneously printed as $\sin \gamma x$.

$$\xi = \xi_0 \cos(\omega t - \varphi). \tag{16}$$

Here

$$\xi_0^2 = k_1^2 + k_2^2,$$

and

$$\tan \varphi = k_2/k_1 = \frac{\omega_0 \delta}{2\pi n}. \tag{17}$$

The phase-angle φ is 90° at resonance, and passes through most of the range from 0° to 180° in the region close to resonance.

§ 4. *Equivalent System with One Degree of Freedom.*—The fact that, with stationary waves, all parts of the rod agree in phase, suggests that a simple method of analysis may be reached by substituting for the actual rod an equivalent system possessing only one degree of freedom. We will therefore consider only the fundamental frequency.

The transition is easily made. In accordance with well-known principles[1] the equivalent mass M is found to be equal to half the actual mass of the rod, or $M = \frac{1}{2}\rho lbe$, these symbols representing density, length, breadth, and thickness respectively.

In place of Young's modulus we use the coefficient of stability, or "equivalent stiffness" g, which, close to the resonant frequency, and when the damping is small, is expressed as

$$g = M\omega_0^2 = \frac{\pi^2 beG}{2l}.$$

This equation follows from the resonance relation $\omega_0 = 2\pi f_0$, and the fact that $c = \sqrt{G/\rho} = 2f_0 l$. M and g correspond to L and $1/C$ in an electric circuit having concentrated, as contrasted with distributed, constants.[2]

The equation of motion is

$$M\frac{d^2x}{dt^2} + N\frac{dx}{dt} + gx = F_0 \cos \omega t. \tag{18}$$

The relation between x, the equivalent displacement, and the actual displacement ξ of the end of the rod, is given below. F_0 is the amplitude of the equivalent impressed force. The resistance factor, N, bears to the viscosity Q the relation $N = \pi^2 \rho beQ/2l$. This is proved by equating the decrement $N/2f_0M$ with the value given in eq. (7).

[1] See, for example, Lamb's Dynamical Theory of Sound, 1910, p. 13.

[2] Strictly, ω_0 is the angular velocity when the amplitude of the *velocity* dx/dt of the equivalent mass M is a maximum under forced vibrations. The maximum amplitude of equivalent *displacement* x comes (under forced vibrations) at the angular velocity $\sqrt{(g/M) - (N^2/2M^2)}$, while the angular velocity of free vibrations is $\sqrt{(g/M) - (N^2/4M^2)}$. The distinction between these three values may under ordinary circumstances be ignored.

The steady-state solution of (18) is

$$x = x_0 \sin (\omega t - \theta), \tag{19}$$

in which the maximum displacement is

$$x_0 = \frac{F_0}{\omega \sqrt{N^2 + \left(\omega M - \frac{g}{\omega}\right)^2}} = \frac{F_0}{\omega N} \cos \theta, \tag{20}$$

and in which

$$\tan \theta = \frac{\omega M - (g/\omega)}{N} = -\frac{2\pi n}{\omega_0 \delta} \tag{21}$$

approximately.

Equation (19) expresses the motion of the rod on what may be termed the "concentrated mass" method, in distinction from the "distributed mass" method first considered. It is easy to show that, near resonance, x and ξ agree in phase (cf. eqs. (17) and (21)). In order to make the amplitudes of x and ξ identical, the force F must be suitably expressed in terms of the impressed stress X_0. To this end, we consider the expression for ξ_0 in (17), and making use of eqs. (7) and (15) and the expressions for P, k, and N, we find that at resonance $\xi_0 = 2X_0be/\omega_0 N$. Upon equating this with the expression for maximum x_0 at resonance from eq. (20), namely $x_0 = F_0/\omega_0 N$, we see that F_0 must have the form

$$F_0 = 2X_0be. \tag{22}$$

This establishes the validity of the method of "concentrated mass," for all cases in which the damping and the range in frequency are both small enough for the expression for g to be satisfied to the desired degree of precision. Equations (19) to (21) are, under the restrictions just named, as accurate as those under the more general theory, and are much more convenient. Their application in the solution of problems with piezo-electric quartz rods, and in particular their use in determining the value of the coefficient of viscosity, must be reserved until later.

Finally, the following simple expression for the displacement of the end of the rod, in terms of the fundamental constants, may be derived from equations (19), (20) and (22), together with the expression for N in terms of Q:

$$\xi = \frac{4X_0 l}{\pi G \delta} \cos \theta \sin (\omega t - \theta).$$

It is easily verified that this equation also follows from equations (16) and (17) according to the more rigorous method of "distributed mass."

WESLEYAN UNIVERSITY,
June, 1921.

THE EFFECT OF FIELD DIRECTION ON MAGNETO-RESISTANCE.

By C. W. Heaps.

Synopsis.

Variation of Magneto-resistance Effect with Direction of the Magnetic Field.—(1) *Theoretical discussion.* The fact that in general the resistance of a conductor differs slightly according to whether the magnetic field is transverse or longitudinal, may be due to two factors. First, there may be a direct effect of the field on the motion of the electrons, as predicted by the electron theories of J. J. Thomson and others. But the author shows that if Townsend's method of developing the electron theory of conduction is adopted, the variation of resistance comes out zero. Second, the effect of the magnetic field may vary with the arrangement of crystals in the conductor, and therefore with the position of the conductor if the crystal structure is anisotropic. (2) *Experiments with cast bismuth, pressed graphite and rolled cadmium* are described in which a small bar or sheet of the material was placed in each of three mutually perpendicular positions in a field of 7,000 or 8,000 gausses, and resistance measurements were made for various positions of the rotatable Weiss magnet. For bismuth and cadmium the variations found are not symmetrical around the current direction and are evidently due chiefly to the crystal structure. For graphite the variations when the field was rotated in the plane of the sheet were within the experimental error, therefore both factors were inappreciable. These results are not conclusive but they suggest that the Townsend theory is correct. If so this magneto-resistance effect may be completely explained by assuming a change in the number and mean free period of the conducting electrons which depends not only on the magnetic field but on its direction with reference to the crystal axes.

When a metallic conductor of electricity is placed in a magnetic field there may be for any given conductor two factors which affect the magnitude of the resulting change of resistance. These two factors are the crystalline structure of the specimen and the angle between the magnetic field and the electric current. Experiments dealing with the latter of these two factors have concerned themselves chiefly with the two cases where the magnetic field is either transverse or longitudinal with respect to the electric current. Lenard [1] found that a longitudinal field produced a smaller resistance increase in a bismuth wire than a transverse field. The writer [2] has obtained a similar result in the case of tellurium, bismuth, lead sulphide, cadmium, zinc, gold, and graphite. Patterson [3] states that his experiments on copper appear

[1] Ann. d. Phys., 39, p. 619, 1890.

[2] Phys. Rev., 10, p. 366, 1917; Phil. Mag., 24, p. 813, 1912.

[3] Phil. Mag., 3, p. 643, 1902.

to indicate a slightly smaller effect for the longitudinal field. Barlow,[1] on the other hand, studying a plate of bismuth, found very little difference in the resistance change for the two directions of the field. The curves given by Barlow seem to indicate that a longitudinal field produces the greater increase of resistance.

The experiments cited above were performed for the most part with specimens of undetermined crystal structure, hence it is conceivable that the crystal structure of the specimens differed for the different directions of the magnetic field. In such a case we cannot say definitely that it is the orientation of the current with respect to the magnetic field which affects the magnitude of the resistance change; it might well be the lack of isotropy of the specimen which produces this effect.

The effect of crystal structure on magneto-resistance has been investigated for graphite by Roberts.[2] Roberts concludes that the resistance increase of this substance is independent of the direction of the electric current with respect to the field, depending only on the angle between the crystal axis and the magnetic field. De Haas[3] experimented with antimony and proved that for this metal the orientation of the crystal axis is of considerable importance. His experiments are not decisive in the matter but he draws the conclusion that the angle between the directions of the magnetic field and of the current is of no importance, at least to a first approximation.

Now if the conclusion of de Haas regarding this question is correct it is a matter of considerable importance in its bearing on the electron theory of metallic conduction. De Haas, considering the free electron theory, says that the influence of the magnetic field on the free paths of the electrons must be considered as negligible, and that such theories as that of J. J. Thomson[4] which try to calculate the phenomenon from the direct effect of the field on the free electrons cannot possibly give the right result. Now it is generally assumed in the literature of the subject that the electron theory of metals does afford an explanation of magneto-resistance, at least for transverse fields and non-ferromagnetic metals. A number of writers[5] following the general method of Sir J. J.

[1] Ann. d. Phys., 12, p. 921, 1903.

[2] Ann. d. Phys., 40, p. 467, 1913.

[3] Konink. Akad. Wetensch. Amsterdam, 16, p. 1110, 1914.

[4] Rapports presentes au Congres International de Physique, III., p. 138, 1900.

[5] E. P. Adams, PHYS. REV., 24, p. 428, 1907.
Gans, Ann. d. Phys., 20, p. 293, 1906.
Livens, Phil. Mag., 30, p. 526, 1915.
Heaps, PHYS. REV., 10, p. 366, 1917.
Richardson, Electron Theory of Matter, p. 439.
Righi, "I Fenomeni Elettro-atomici," p. 401.

Thomson have derived expressions for the increase of resistance of a metal when placed in a transverse magnetic field. These expressions involve the relation

$$\frac{dR}{R} = C\left(\frac{e}{mu}\right)^2 \frac{l^2}{v^2} H^2, \tag{1}$$

where dR is the increase produced in the resistance R by the magnetic field H, e/m is the ratio of the charge to the mass of the electron, l is the mean free path of the electron, v is its velocity of agitation, and C is a constant depending on the type of theory adopted. Properly speaking, this expression for dR/R refers only to the increase of resistance produced when a longitudinal field is rotated into the transverse position and when the specimen is isotropic. It cannot be supposed, therefore, that calculations of mean free paths, etc., by the use of this formula will be of much value when experimental results are obtained from specimens of unknown crystalline structure or when the dR/R of the above formula is taken to represent the entire effect of a transverse field as was the case in Patterson's calculations.

If the conclusions of de Haas are correct, *i.e.*, that there is no intrinsic difference between the effects of a transverse and a longitudinal field, then we should expect the theoretical expression for dR/R of equation (1) to come out equal to zero. As a matter of fact, one form of the theory gives this result, as may be shown in the following manner.

Let us adopt the ordinary assumptions of the free electron theory of metals, assuming collisions between electrons and molecules to be like those between hard elastic spheres. With these conditions J. S. Townsend has developed an expression for the velocity with which a group of free electrons drifts through an aggregation of molecules under the combined influence of electric and magnetic fields.[1] In addition to assuming elastic collisions Townsend neglects persistence of velocities, assumes that the free periods of electrons may vary from zero to infinity, and lets the number of free periods, out of a total number N, comprised in the time interval between t and $t + dt$ be equal to $(N/T)e^{-t/T}dt$, where T is the mean free period.

If the magnetic field H acts along the z axis and the electric fields X and Y act along the x and y axes, respectively, Townsend's theory gives for the drift velocities U and V along the respective x and y axes:

$$U = \frac{e}{m} T \frac{(X - Y\omega T)}{1 + \omega^2 T^2}, \tag{2}$$

$$V = \frac{e}{m} T \frac{(Y + X\omega T)}{1 + \omega^2 T^2}, \tag{3}$$

[1] Electricity in Gases, p. 100.

where $\omega = He/m$. In Townsend's development Y is assumed zero. It is to be noted that the deduction of the above formulæ does not involve approximations like those made in the references cited above, where other methods are used.

If we consider a plate of metal lying in the x, y plane and carrying a current along the x direction the condition that there shall be no current along the y direction requires V to be zero. There must, therefore, exist an electric field given by $Y = -X\omega T$ in the metal to prevent the electron current along y. It is the potential difference due to this field which is observed as the Hall effect.

If we substitute this value of Y in equation (2) we get

$$U = X\frac{e}{m}T. \tag{4}$$

Hence the drift velocity along x under these conditions is not affected by H so long as T remains unchanged. The current density along x is given by

$$I = neU = \frac{ne^2}{m}XT, \tag{5}$$

where n is the number of free electrons per unit volume. Thus if n, T, and X are not functions of the magnetic field, the current I is independent of H and we have

$$\frac{dR}{R} = 0. \tag{6}$$

We may now consider a form of conductor in which $Y = 0$. Let the current enter at the center of a flat circular plate and leave it at its periphery, and let the plane of the plate be normal to H. This is the arrangement used by Corbino.[1] Under these conditions the magnetic field causes a circular current to flow in the plate, and since there is no banking up of electrons to produce the Hall e.m.f. we may assume that Y, taken as perpendicular to a radius, is zero. In this case the radial current may be represented by

$$I_r = neU = \frac{ne^2}{m}X\frac{T}{1 + \omega^2T^2}. \tag{7}$$

Hence

$$\frac{I_0 - I_r}{I_r} = \frac{dR}{R} = \omega^2T^2, \tag{8}$$

where I_0 is the current when H is zero. Thus with the Corbino arrangement the specific resistance of the metal will be found greater than in

[1] Phys. Zeits., 12, pp. 561, 842, 1911.

the case where the Hall e.m.f. is allowed to develop. Under the ordinary conditions of measuring magneto-resistance, however, the Hall e.m.f. is always present, so it is not permissible to assume $Y = 0$ in developing the theory, as has been done by many previous writers.

It thus appears according to Townsend's theory that there should ordinarily be no change of resistance produced in a metal by the direct action of the magnetic field on the motion of the electrons between collisions. Townsend's theory is therefore in agreement with the conclusions of de Haas.

The theory of magneto-resistance has been worked out by Gans and by Livens.[1] These writers follow the method of H. A. Lorentz in assuming a slight departure from Maxwell's law of distribution of velocities among the electrons. The effect of the Hall e.m.f. is not neglected. The formula obtained by Gans for small magnetic fields is

$$\frac{dR}{R} = \frac{12 - 3\pi}{8}\left(\frac{e}{m}\right)^2 \frac{l^2}{v^2} H^2. \tag{9}$$

This formula assumes collisions to be like those between elastic spheres and here also only the difference between the effect of a transverse and a longitudinal field is contemplated. Thus the theory of Gans does not agree with the conclusions of de Haas. Livens assumes molecules to act as centers of force and gets a more general formula. He points out that if the potential energy of an electron repelled by a molecule at a distance r is given by $m/2 \cdot (\mu/r)^s$ then when $s = 4$ the value of dR/R should be zero.[2] It appears therefore that if de Haas is correct in his conclusions regarding experiment—*i.e.*, that the difference between the longitudinal and transverse magneto-resistance effects is zero—then the theory of Livens demands a special type of field around a molecule. If on the other hand we adopt Townsend's method of handling the problem then the molecules and electrons may act like solid elastic spheres and we still get agreement with the conclusions of de Haas.

It seemed to the writer that further experiments were necessary in order to establish a theory, hence the effect of the direction of the magnetic field on the resistance of bismuth, graphite, and cadmium has been investigated. The magnetic field was furnished by a large Weiss electromagnet capable of being rotated about a vertical axis. The angular position of the magnet could be read from a scale at the base of the instrument. The pole-pieces were 10 cm. in diameter and were set so that the faces were 3.03 cm. apart. The specimen to be examined was

[1] L.c.

[2] The formula of Livens reduces to that of Gans if $s = \infty$.

supported between the pole-pieces so that the electromagnet could be rotated without disturbing it. This specimen was inserted in one arm of a Wheatstone bridge, balancing being accomplished by a shunt arrangement somewhat after the fashion described by Crandall.[1] A Leeds and Northrup moving coil galvanometer of resistance 13 ohms and sensitivity 11 mm. per microvolt was used. Since the current through the electromagnet had a value of 8 or 10 amperes, and since no special precautions were taken to maintain constancy of temperature, the resistance of the specimen was found to change very slowly during the time required to obtain a set of observations. A correction for this temperature effect was made by periodically repeating a standard resistance measurement of the specimen and assuming a linear resistance change during the interim between these periodic measurements. As a matter of fact when a set of observations was taken with reasonable rapidity no very great error was introduced by temperature effects. The bridge current was made as small as was convenient—of the order of 0.01 ampere—and was kept flowing during the whole time of taking a set of observations.

The process of making observations consisted in balancing the bridge with the specimen between the poles of the magnet but with no exciting current flowing. The magnetizing current was then set up and a new balance of the bridge obtained. With this magnetizing current kept constant the bridge was balanced for different angular positions of the electromagnet and values of $\delta R/R$—which is here the total increase of resistance of the specimen divided by the resistance in zero field—were calculated for these various positions of the magnet. In calculating $\delta R/R$ the resistance of the copper wires leading to the specimen was carefully allowed for, though it was unnecessary to consider the effect of the field on the resistance of these leads since copper shows very small magneto-resistance effects. When the specimen was removed from between the poles it was found that revolving the magnet did not affect the bridge balance. Spurious effects, such as the influence of the magnet on the zero position of the galvanometer can thus be considered as negligible.

The bismuth used in this investigation was rated by Merck as about 98 per cent. pure. A specimen was made by cutting a thin bar of rectangular cross-section from a thin plate of cast bismuth. The dimensions of this bar were roughly $1.1 \times 0.15 \times 0.05$ cm., the shortest dimension being perpendicular to the plane of the original large plate of metal. Experimental results for this bar are given in Fig. 1, where the

[1] PHYS. REV., 2, p. 343, 1913.

lenght of the radius vector from 0 to any point of a curve is set equal to $\delta R/R$ and the angular position of this radius vector is determined by the orientation of the magnet. Results are plotted only for positions of the magnet comprised between 0° and 180°, as duplication results in the case of larger angles. The field strength was 7,000 gausses and the temperature was that of the room—about 23° C.

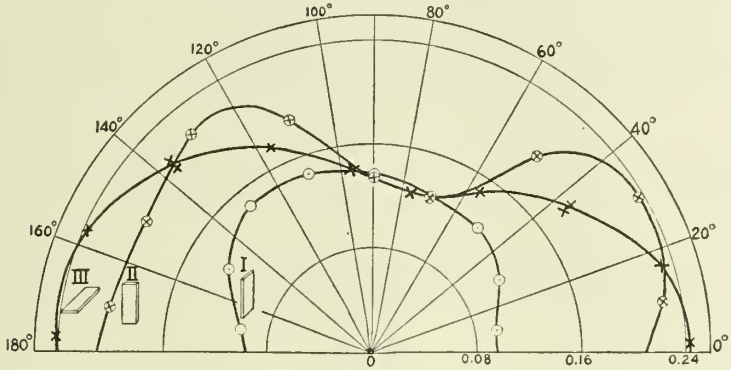

Fig. 1.

Three curves were obtained for this specimen, corresponding to three different settings of the bar between the poles of the magnet. The three-dimensional diagrams of the bar placed beside the respective curves will make the arrangement clear. The magnetic field is always in a horizontal plane, the plane of the figure. In curve I. the length and thickness of the bar are in this horizontal plane, the breadth in a vertical plane. The magnetic field for this curve was thus always perpendicular to the breadth of the specimen. In curve II. the breadth and length of the bar were in a horizontal plane; the magnetic field was thus always perpendicular to the shortest dimension of the specimen. In curve III. the breadth and thickness of the specimen were in a horizontal plane; the magnetic field was here, therefore, always perpendicular to the length of the specimen and to the current. It will facilitate interpretation of the curves to note that the relative orientation of field and specimen may be determined for any point on the curve by imagining the diagram of the specimen to be shifted without rotation to the desired point of the curve.

The lack of symmetry of these curves is an indication of a complex crystalline structure in the bar. Curves I. and II. coincide, within the limits of error of the experiment, at the angle 90°. This coincidence is, of course, to be expected, for at this point the relative arrangement of specimen and field is identical for the two curves. Curve III. should

coincide with curve II. at 0° and 180° for the same reason. Similarly curve III. should have the same value at 90° as curve I. at 0° and 180°. The fact that curve III. does not have these values ($\delta R/R$ being too great in each case) is very probably due to a slight error in measuring lead resistances, for in setting the specimen for III. after I. and II. had been obtained it was necessary to disconnect the old leads and put on new ones. The specimen itself had a very small resistance—about 0.05 ohm—while the resistance of the leads was 0.0442 ohm. The Wheatstone bridge, though sensitive to changes of resistance, was not very accurate for the measurement of absolute values of small resistances. Slight inaccuracies in measuring these small resistances would affect the calculated value of $\delta R/R$ but would be of no consequence in making comparisons along any one curve. Another cause of error might lie in the altered resistance of the soldered joint between lead wire and specimen. No measurement of this junction resistance could be easily made. A third cause of error lies in the difficulty of setting the specimens accurately in position.

Certain general conclusions may be drawn from the curves of Fig. 1. In curve I. the effect of a longitudinal field (measured by the length of the radius vector at 90°) is greater than the effect of a transverse field (measured by the length of the radius vector at 0°). For curve II. the converse is true. It appears obvious that crystalline structure plays a very important rôle in the phenomenon of magneto-resistance. Since curves I. and II. are not symmetrical with respect to the 90° position (the direction of current flow) we must conclude that crystalline structure is producing a distortion of the curves. It thus appears impossible in this bismuth specimen to separate the effect due to current direction—if there is such an effect—from the effect due to crystal structure. We may conclude, however, that crystalline structure is a very important factor because curve III. obtained with the current always transverse shows great variations as the field changes direction. The conflicting results of Barlow and Lenard cited above can now be explained as arising solely from the different arrangement of crystalline axes with respect to the field. The complicated nature of the results obtained with bismuth might have been foreseen from the work of E. van Everdingen[1] who found that when a bismuth crystal is placed in a magnetic field of arbitrary direction its resistance may be represented by an ellipsoid with three unequal axes. In general, then, a cast bismuth plate is not apt to possess a plane in which a magnetic field may alter its direction without encountering dissimilar crystalline conditions.

[1] Konink. Akad. Wetensch. Amsterdam, III., p. 407, 1991.

Some further experiments were performed on wire made by forcing molten bismuth into a vertical capillary tube. It might be expected that for all directions of a magnetic field perpendicular to the wire the same magneto-resistance effect would be noted. Such, however, proved not to be the case, a small but unmistakable dissymmetry being observed. When the specimen was placed horizontally and the magnet rotated from the transverse to the longitudinal position the latter position was found to give the smaller effect. The greatest increase of resistance was observed when the magnetic field made an angle of 72° with the length of the wire.

For the experiments on graphite the specimen was made from the ordinary powdered graphite, consisting of small crystalline particles, which is used for lubricating purposes. This powder was compressed by means of a hydraulic press into the form of a thin plate on the top of an ebonite block. The graphite was made to adhere to the ebonite by a thin coat of beeswax and resin which had been previously applied to the ebonite. Two brass screws had been set into the block with their heads flush with its surface, so that by cutting away part of the graphite plate with a razor blade a thin bar was obtained with its ends resting in close contact with the screw heads. Copper wires were soldered to the ends of the screws and used for connecting the specimen into the Wheatstone bridge. The dimensions of the bar were roughly 1.2 × 0.15 × 0.03 cm. and its resistance was 1.15 ohms at 26.5° C. This resistance increased in one week to 1.23 ohms. Probably this increase was due to gradual readjustment of strains in the specimen.

The curves of Fig. 2 represent results obtained with this graphite in a

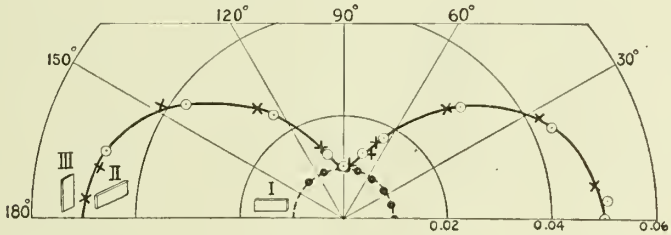

Fig. 2.

field of 8,000 gausses. The orientation of the specimen for any particular set of observations is represented diagrammatically as in the previous case with bismuth. It appears from curve I. which is practically a semicircle, that as long as the magnetic field is in the plane of the specimen we get the same change of resistance irrespective of the direction of the

field. There is a slight deviation of the points from the curve. It is so slight, however, as not to show up in the graph and is probably caused by inaccurate setting of the specimen. The points for curve II. are marked with crosses, those for curve III. with circles. These two curves coincide to a fair degree of accuracy. The obvious interpretation of the curves is as follows.

In the plane of the specimen the arrangement of the small crystals is such that any direction in this plane is the same as any other direction as far as the average crystalline structure is concerned. If this is the case then the circular nature of curve I. implies that the direction of the electric current is of no importance as regards the magnitude of the resistance change produced by the magnetic field. Curves II. and III. indicate that the average crystalline structure in a direction perpendicular to the plate is different from that parallel to the plane of the plate, but the fact that these two curves coincide is again evidence that the change of resistance is independent of the relative directions of field and current.

The conclusions which Roberts[1] reached in his study of large graphite crystals are corroborated by the above experiments on a conglomerate. In the writer's previous work with graphite powder[1] it was concluded that $\delta R/R$ for a transverse field was greater than that for a longitudinal field by 8×10^{-4}. Differences of that order of magnitude were obtained in the various observations of curve I., but it seems probable that these differences were the result of experimental errors arising from temperature changes or inaccurate adjustment of the specimen. The longitudinal field of curve I. gave a value of $\delta R/R$ greater by 1.5×10^{-4} than the $\delta R/R$ of the transverse field. It is difficult to adjust such small specimens accurately with respect to the magnetic field and a small deviation from accuracy can produce quite large changes in $\delta R/R$. Possibly the writer's previous results can be explained as due to inaccurate adjustments.

The experiments on cadmium were performed on a specimen made as follows. A disk of the metal was sawed from a round bar. This disk was put through a rolling mill a number of times, and always in the same direction so that finally a long thin sheet of cadmium was secured. A section of this sheet was then cemented with wax flat upon a glass plate and cut with a razor into the form of a grid 0.9 cm. wide and 2.5 cm. long, containing 16 strips of cadmium connected in series and having a total resistance of 1.71 ohms. This grid was supported between the poles of the magnet in a horizontal position and examined for magneto-resistance in a field of 7,600 gausses. A fairly large bridge current had to be used with this metal in order to get sufficient sensitivity, so that troublesome

[1] L.c.

temperature effects were introduced. However, by taking in rapid succession a number of observations for the transverse and longitudinal positions of the magnet it was found that $\delta R/R$ for the transverse field was greater by 2.1×10^{-5} than for the longitudinal field. The specimen was then placed so that the strips of the grid were vertical, the field being always transverse to the current. A series of observations was taken with the field alternately perpendicular and parallel to the plane of the grid. It was found that $\delta R/R$ was greater by 5.2×10^{-5} for the perpendicular field than for the field parallel with the surface of the grid. Since the current was here always transverse to the field it is to be concluded that differences of crystalline structure are responsible for the difference of 5.2×10^{-5}. As regards the difference of 2.1×10^{-5} this might be due either to differences of current direction or to the anisotropic character of the strips.

In previous work by the writer on cadmium strips made by hammering no difference was detected in $\delta R/R$ for a transverse field whether normal or parallel with the surface of the strips, while a longitudinal field was found to produce a smaller effect than the transverse field. If this specimen made by hammering was really isotropic as regards magnetic effects then it appears that the current direction is a factor in determining the resistance change of cadmium. It cannot be said with certainty, however, that such an isotropic character was produced by this method. On the other hand, rolling the specimen does introduce an anisotropic character. Since the drawing of metal into the form of wires is more analogous to the rolling method than to the hammering method we might expect that cadmium wires would exhibit magneto-resistance effects for a longitudinal field which are different from those for a transverse field solely because of the anisotropic nature of the wires. We cannot say, therefore, that experiments which have been performed on cadmium have either proved or disproved the theory of magneto-resistance outlined above. Tests of other metals such as zinc, gold, copper, etc., could not be made because of insufficient sensitivity of the apparatus.

The general conclusions to be drawn from the above experiments are as follows. Influences of crystal structure are so great in the metals bismuth and cadmium that any effect arising from the direction of the current cannot be differentiated from effects arising from crystal structure. In the case of graphite, if the direction of the electric current with respect to the magnetic field is of any importance at all in changing the magnitude of magneto-resistance effects then any such resulting change is very small compared with the effect of crystal structure on magneto-

resistance. The experiments with graphite may be considered as supporting the correctness of equation (6). If equations such as (9) hold true it must be supposed that l/v is very small, at least in graphite. On the whole, one must conclude that calculations such as those of Patterson, in which electron concentrations and mean free periods of electrons in different metals are determined from measurements of magneto-resistance, are by no means to be relied upon. The effect of crystal structure is too vital a factor to neglect. Furthermore the theory as developed above by Townsend's method indicates that there should ordinarily be no effect of a magnetic field on resistance (provided this effect is limited to direct action on the electrons' motion) and it appears that there is some experimental evidence in support of this theory. If we adopt the Corbino arrangement, however, and use equation (8) it is possible to calculate the mean free period of the electrons in the metal. Essentially this method has been used by the writer in a previous paper,[1] and it is perhaps surprising that the results obtained agree as well as they do with the results calculated by Patterson from J. J. Thomson's equation.

Suppose now that we consider equation (6) as essentially correct, that is, suppose a magnetic field does not alter the resistance of a metal by virtue of any direct action on the motion of an electron between collisions. Then in order to explain the change of resistance observed experimentally we shall have to consider the factors of equation (5) and determine which are functions of the magnetic field. It is conceivable that the electric field X in the region where the electrons move may be modified by the action of the magnetic field on the molecules of the metal. If polarization electrons play any part in modifying the internal field [2] it is not impossible that a magnetic field, say by changing the orientation of molecular magnets, should affect this field produced by the polarization electrons. However, since there appears to be no relationship between the direction of the magnetic field with respect to X and the resistance increase which this field produces in the metal, it seems safe to say that X is not dependent on H. The average distance between molecules is probably changed by a magnetic field [3] so that the free period T will depend on H. It has been suggested by a number of writers[4] that n should be affected by a magnetic field. If we imagine in the metal a system of electrons moving in open and closed orbits—

[1] PHYS. REV., 12, p. 340, 1918.

[2] See Richardson, Phil. Mag., 23, p. 614, 1912.

[3] See E. P. Adams, l.c.

[4] E. van Everdingen, Konink. Akad. Wetensch. Amsterdam, III., p. 177, 1900.
La Rosa, N. Cim., 18, p. 39, 1919.
Heaps, l.c.

as suggested by Richardson[1]—it is not difficult to understand why a magnetic field might alter equilibrium conditions in such a system and thus change n.

If we let n_0, T_0, and I_0 be the respective values of n, T, and I when the magnetic field is zero then

$$I_0 = n_0 \frac{e^2}{m} X T_0. \tag{10}$$

Combining this equation with (5) gives

$$\frac{I_0 - I}{I} = \frac{\delta R}{R} = \frac{n_0 T_0}{nT} - 1. \tag{11}$$

This equation, in the light of Townsend's theory, is probably the most general expression for magneto-resistance. The factor given by equation (1) does not appear. It is to be noted that both n and T may depend upon the direction of the field in a metallic crystal as well as upon the magnitude of the field.

The experimental work described in this paper serves to emphasize the importance of crystal structure in relation to magneto-resistance. The question might well be asked as to whether crystalline structure is not essential to the production of the phenomenon. Becker and Curtiss[2] have found that bismuth films made by cathode sputtering, and therefore presumably amorphous, show no magneto-resistance effects until after they have been subjected to a heating process which crystallizes the metal. As far as the writer is aware, a magnetic field has never been found to change the resistance of a strictly non-crystalline substance,[3] so it is not impossible that an orderly arrangement of the molecules is essential for the manifestation of the phenomenon. The settling of this question, however, requires more extensive experimental data than is available at present.

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[1] Electron Theory of Matter, p. 463.

[2] Phys. Rev., 15, p. 457, 1920. See also Richtmyer and Curtiss, Phys. Rev., 15, p. 467, 1920.

[3] Patterson found an effect with liquid mercury but later work (see Zahn, Jahrbuch der Radioaktivität und Elektronik, 5, p. 197, 1908) indicates that the observed increase of resistance is to be ascribed to electrodynamic actions.

ON THE PRINCIPLE OF COMBINATION AND STOKES' LAW IN THE X-RAY SERIES.

By D. Coster.

Synopsis.

New X-Ray Line γ_6 for Elements Tantalum to Uranium.—The two emission lines γ_2 and γ_3 are found to be in reality three lines. The new line γ_6 has *wave-lengths* of 1110, 1072, 842, 630 and 593 $\times 10^{-11}$ cm. for Ta, W, Tl, Th and U respectively. In the cases of Ir, Pt and Au it is too near γ_2 and in the cases of Pb and Bi too near γ_3 to be separated.

New Absorption Lines of the M-series.—Ma_1, Ma_2 and Ma_3 have been measured for *bismuth*, and Ma_4 and Ma_5 for *thorium and uranium*, the *wave-lengths* being, respectively, 4762, 4569, 3894, 2571, 2388, 2385 and 2228 $\times 10^{-11}$ cm.

Identification of the Line for Tantalum and Tungsten.—For all the elements Os to U, the difference in wave-lengths of $\beta_2 - \beta_5$ is equal to about 29 $\times 10^{-11}$ cm. If this difference is the same for Ta and W also, the β_5 lines for these elements must be the lines 1220.8 and 1250.6, respectively, instead of those ordinarily assumed.

Measurement of La_1 and La_2 for Tungsten by a different method gave the same wave-lengths as those found by Duane and Patterson.

Relationships between Emission and Absorption X-Ray Spectra.—(1) *Stokes's law* seemed not to hold in the case of W. It was thought the apparent discrepancies might be due to an error in the measurement of La_1 and La_2, but these measurements were found correct; however, the discrepancies disappear if we identify β_5 with 1220.8 instead of 1212.5 and if we associate γ_2 and γ_3 with La_3 and the new line γ_6 with La_2. (2) *Relations between frequencies.* The frequencies of seven of the L-series lines are each approximately equal to the difference between the frequency of an La-line and that of an Ma-line.

In a previous note I called attention to the fact that Stokes' law holds for the L-series of the elements Pt – U. For W however the limiting wave-lengths La_1 and La_2 seemed to be much larger than the wave-lengths β_5 and γ_2 respectively; and I suggested a possible source of error in the method by which Duane and Patterson determined the absorption-wave-lengths of tungsten. On account of the great theoretical importance of this matter I have repeated the measurements, but with essentially the same result as these authors. To avoid every kind of complication I proceeded in the following manner. Use was made of a water-cooled bulb with aluminium-cathode, constructed by Prof. Siegbahn and described by A. Hadding.[1] This bulb has the great advantage

[1] Zeitschrift für Physik, *3*, 369, 1920.

that the slit of the spectrograph can be placed very near to the anticathode. It was driven with a current up to 15 *mA* and a tension of about 40 *kV*. First the absorption spectrum was taken with an iron anticathode and the absorbing substance placed between the bulb and the slit. Part of the slit was covered with a thick lead screen, so that only the upper part of the plate was exposed. In order to eliminate effects due to inhomogeneities of the absorbing screen, this was turned round during the exposure. Then the iron anticathode was replaced by a tungsten one, the absorbing substance was removed and by a suitable adjustment of the lead screen an emission-spectrum could be obtained on the lower part of the same plate. The plates demonstrated quite obviously that the absorption wave-lengths are considerably larger than the wave-lengths thus far denoted by β_5 and γ_2. For purposes of control the La_2 and the $L\gamma$-lines of gold and lead were taken in the same way; but, as might be expected, no such a difference was found here.

Now we may escape from the theoretical difficulty lying in an exceptional condition of the tungsten-spectrum by assuming, as already has been done by Hoyt[1] and by Dauvillier,[2] that the β_5-line of this element has not as yet been identified accurately. As may be seen from Table I.

Table I.[3]

	U.	Th.	Bi.	Pb.	Tl.	Au.	Pt.	Ir.	Os.	W.	Ta.
$\beta_2 - \beta_5$ . .	28.58	28.49	30.63	30.48	29.56	29.55	29.40	29.87	28.38	29.41	30.32

the wave-length difference $\beta_2 - \beta_5$ is nearly constant from U down to Os. If now we take for β_5 of W the line 1212.8 and for Ta the line 1250.6 then for these elements the difference $\beta_2 - \beta_5$ likewise remains nearly the same.

As regards the line γ_2, the situation is more complicated than could be anticipated formerly. Recently I have taken new photographs of the emission lines of the elements Ta – U with the same metal bulb.[4] I find, that instead of the lines thus far denoted by γ_2 and γ_3, we must assume three lines.[5] One of these, which we may call γ_6, lies at a constant wave-length-distance from γ_1. The frequency-difference $\gamma_{\gamma 6} - \gamma_{\beta 5}$ is

[1] Proc. Nat. Ac. Sc. Washington, Nov., 1920.

[2] Comptes Rendus, 11 April, 1921.

[3] The wave-lengths are given in cm. $\times 10^{-11}$.

[4] See Zeitschrift für Physik, *6*, 158, 1921.

[5] An analogous hypothesis was pronounced some time ago in a letter from Mr. Wentzel to the author.

the same as the difference $\gamma_{\beta 1} - \gamma_{\alpha 2}$. For the elements Ta and W, γ_6 is of very small intensity relatively to the other γ-lines; but, in the neighborhood of Pt there is a sudden rise in its intensity. A similar change has been observed for β_5. Moreover, there are two lines γ_2 and γ_3, which lie at about the same wave-length-distance from one another and which both have about the same intensity. Only for the elements Ta, W, Tl and U was γ_6 separated from the lines γ_2 and γ_3, but where complete separation did not occur, a corresponding broadening and darkening of γ_2 or of γ_3 could usually be observed.

TABLE II.

	γ_1	γ_6	γ_2	γ_3	$\gamma_1 - \gamma_6$	$\gamma_2 - \gamma_3$
U	612.83	592.6	604.4	597.0	20.23	7.4
Th	651.03	630.1			20.93	
Bi	810.65	787.4	792.9	787.4	23.25	5.5
Pb	837.08	813.70	818.2	813.70	23.38	4.5
Tl	865.29	841.7	844.7	837.9	23.59	6.8
Au	924.37	901.25	901.25	859.68	23.12	5.57
Pt	955.45	931.7	931.7	925.6	23.75	6.1
Ir	988.41	963.6	963.6	956.6	24.8	7.0
W	1,095.53	1,072.0	1,065.84	1,059.65	23.53	6.19
Ta	1,134.71	1,110.0	1,102.0	1,096.2	24.71	5.8

In Table II. the wave-lengths of the lines γ_1, γ_6, γ_2 and γ_3 and the wave-length-differences $\gamma_1 - \gamma_6$ and $\gamma_2 - \gamma_3$ are given in cm. 10^{-11}. It seems to be most probable that only γ_6 is connected with the La_2-discontinuity, whereas γ_2 and γ_3 both belong to La_3.

Thus far only three absorption-discontinuities Ma_1, Ma_2 and Ma_3 in the M-series of U and Th were known, these corresponding to the measurements of Stenström. I have succeeded in measuring two other discontinuities Ma_4 and Ma_5 of shorter wave-length of U and Th and Ma_1, Ma_2 and Ma_3 of Bi, with the following provisional results:

TABLE III.

	Ma_1	Ma	Ma_3	Ma_4	Ma_5
U	3,491	3,326	2,873	2,385	2,228
Th	3,721	3,552	3,058	2,571	2,388
Bi	4,762	4,569	3,894		

The values for Ma_1, Ma_2 and Ma_3 of U and Th were taken from Stenström's dissertation. As is seen from Table IV. the frequencies of the lines l, η, α_1, α_2, β_1, β_3 and β_4 are each equal to the difference of an L-absorption-frequency and a M-absorption-frequency.

TABLE IV.[1]

	1	$L\alpha_1-M\alpha_5$	η	$L\alpha_2-M\alpha_5$	α_1	$L\alpha_1-M\alpha_1$	α_2	$L\alpha_1-M\alpha_2$
U.....	855.84	855.1	1,134.95	1,131.8	1,003.23	1,002.17	990.37	989.21
Th.....	819.19	818.8			955.78	954.80	944.08	943.15
Bi.....					789.54	797.43	790.20	789.35

	β_1	$L\alpha_2-M\alpha_2$	β_3	$L\alpha_3-M\alpha_3$	β_4	$L\alpha_3-M\alpha_4$
U.....	1,269.08	1,265.87	1,286.29	1,285.78	1,222.53	1,220.86
Th.....	1,194.94	1,193.15	1,211.67	1,209.77	1,155.00	1,151.86
Bi.....	959.93	958.16	973.85	975.86		

Apart from the accidental errors there seems to be a systematic deviation between the line-frequency and the difference of the absorption-frequencies, so that we may conclude that there must be a small systematical error either in my measurements of the lines or in the work of Duane and Patterson. If this is the case, it is most probable that the same error should be found in the measurements of all the elements. We should therefore be inclined to conclude that for the elements Pt, Au, Tl, Pb and Bi, and perhaps for W also, the absorption-wave-lengths are a little shorter than the corresponding wave-lengths β_5 and γ_6 and that the difference should correspond to a difference of about 5–10 volts.

A superficial examination of my plates does not give the impression that the absorption-wave-lengths are shorter than the corresponding emission-wave-lengths. But the selective absorption commences with a faint white line, which may be tentatively considered as an image of the slit just as the black emission-lines are. This shows that the electron "prefers" the absorption of a very definite wave-length, which is at the same time the smallest frequency it is able to absorb. To estimate this frequency we are to measure the middle of the white absorption-line relatively to the middle of the black emission-lines. I hope to have later the opportunity to study this problem with the required accuracy with the photometer-method.

It gives me great pleasure to express my thanks to Professor Siegbahn, who put the apparatus of his laboratory at my disposal and advanced the work by his great interest.

LUND, SWEDEN, PHYS. LAB. OF THE UNIVERSITY,
June, 1921.

[1] The frequencies have been calculated in multiples of the Rydberg constant (limiting frequency of the Lyman series of hydrogen).

THE MOBILITY OF ELECTRONS IN PURE NITROGEN.

By Leonard B. Loeb.

Synopsis.

Mobility of electrons in pure nitrogen was determined, using the Rutherford alternating potential method, for pressures ranging from *75 to 600 mm.*, for frequencies ranging from *7,000 to 150,000 cycles* (obtained from an audion oscillating circuit), and with electric fields of from 10 to 100 volts/cm. Reduced to atmospheric pressure the mobility found is of the order of 10,000 cm. sec.,/many times the highest value previously obtained, and it was observed to vary with pressure and electric field according to the equation $K = 571{,}000/(21 + 760\ V/pd)$, where V/d is in volts/cm. and p in mm. of Hg. A discussion of the possible sources of error shows that none can be responsible for this variation with V/pd, and the form of the mobility curves confirms this variation. A *theoretical interpretation* of these results on the basis of the Townsend equation for electron mobility leads to the conclusions: that if the Townsend theory is correct (1) either the *energy lost at each impact* of an electron with a nitrogen molecule or the *mean free path* must be a function of V/pd, and (2) in either case the mean free path for velocities of the normal agitation must be about 22 times the mean free path of the gas molecules instead of $4\sqrt{2}$ times, as given by the kinetic theory.

I. Introduction and Previous Results.

THE results obtained in a study of the attachment of electrons to neutral molecules to form negative ions,[1] indicated that the mobility constant for the electrons in a gas at atmospheric pressures was apparently not constant. It thus became of interest to determine the mobility of electrons in gases in which they move unattached to molecules at atmospheric pressures in order to discover what conditions govern the variations of mobility. The mobilities of electrons in pure argon and nitrogen at atmospheric pressures were first determined by Franck,[2] who obtained 206 cm./sec. for the highest value in the former and 145 cm./sec. for the highest value in the latter gas. Haines[3] measured the mobilities of electrons in nitrogen and found mobilities as high as 506 cm./sec. while the average value obtained lay at about 367 cm./sec. In hydrogen he found the highest value to be 170 cm./sec. Finally

[1] Loeb, L. B., Phys. Rev., Vol. XVII., No. 2, pp. 106–107, Feb., 1921.

[2] Franck, J., Verh. d. Deut., Phys. Ges., 12, p. 613, 1913.

[3] Haines, Phil. Mag., 6, 30, p. 503, 1915.

Wellisch[1] working with what he thought were purely electronic carriers in CO_2 obtained mobilities which varied from 256 cm./sec. to much lower values. In H_2 he got a value of 1,700 cm./sec. for the mobility.

II. Experimental Method.

In the present work the mobilities were determined on the photo-electrons liberated from a brass plate (P), Fig. 1, struck at grazing incidence by ultraviolet light from a quartz mercury arc, using the Rutherford alternating current method. The experimental method of making the determinations was essentially the same as that used by the writer in an earlier[1] paper on negative ions. The gas used was pure nitrogen in which it has been shown that the electrons do not attach to form[2] ions.[5] The method of purification was carried out as described in the paper[5] showing this to be the case. A reduction of the contamination of the gas while in the measuring chamber by vapors arising from sealing waxes and organic materials used in closing the chamber was accomplished by the use of a new ionization chamber. It was similar to the one previously described, except that the rubber gasket was replaced by a ground steel joint with a mercury seal.

The mobilities were measured by the use of the high-frequency oscillations from two vacuum tube oscillators of the Western Electric "E" tube type operating in parallel. The circuits used are shown in the diagram, Fig. 1. In some cases the oscillations were taken directly off the primary condenser, and led to the plate P of the measuring system. In many others they were taken from the condenser of a secondary circuit closely coupled to the primary circuit, and tuned to resonance with it. The alternating potential was varied in the measurements by changing the resistance (r) in the plate circuit of the oscillators. This change in the resistance resulted in a gradual change in the frequency with the voltage, sometimes causing a reduction in frequency as the voltage decreased and at other times causing an increase, depending on the constants of the oscillating circuit used at the time. It therefore became necessary to measure the frequency of the oscillations at several values of the voltage in order to obtain accurate values of the mobility. This was done with a wave meter. The frequencies thus obtained appeared to be in good accord with those computed from the circuit constants, where computation was possible. The alternating potentials were measured with Kelvin type static voltmeters which were calibrated from time to time against a standard Weston voltmeter. A large number

[1] Wellisch, E. M., Am. Jour. Science, July, 1915.

[2] Loeb, L. B., Proc. Nat. Acad. Sciences, 6, No. 7, pp. 335–441, July, 1920.

of mobility curves were taken covering frequencies ranging from 30,000 cycles up to 150,000 cycles per second, and pressures of nitrogen from 600 mm. to 75 mm. of Hg. It was found possible to study the mobility curves with potentials which varied from 20 volts to 140 in all cases, and from 30 volts to 300 in a few cases. Below 20 volts it was not satisfactory to make mobility measurements as the oscillations became rather unsteady, though some determinations were carried down to less than ten volts. The plate distances *PE* used in the measuring chamber were 2 cm. and 1.5 cm.

III. Results.

In Figs. 2 and 3 are given some of the typical mobility curves, obtained

Electron Mobility Curves, Current Plotted against Voltage.

No.	Press. in Mm. p.	Frequency n.	Intercept Corrected V_0	Mobility u.	Mobility Constant K.
1.....	610	28,000?	7.6	34,800	28,000
2.....	597	31,800	14.3	21,000	16,500
3.....	607	49,200	24.8	17,350	13,850
4.....	599	53,100	28.5	17,600	13,700
5.....	615	62,200	32.6	17,900	14,600
6.....	606	68,000	40.1	14,850	11,850
7.....	604	76,000	57.3	11,600	9,230
8.....	599	75,000	66.8	10,650	8,400
9.....	625	95,500	80.1	11,100	9,200
10.....	603	82,200	90.7	8,600	6,800
11.....	597	88,000	94.0	8,200	6,440

Electron Mobility Curves, Current Plotted against Voltage.

No.	Press. in Mm. p.	Frequency n.	Intercept Corrected V_0	Mobility u.	Mobility Constant K.
1.....	302	82,000	38.7	18,000	7,340
2.....	303	98,000	74.4	11,500	4,610
3.....	166	93,000	32.4	25,100	5,500
4.....	166	115,000	104.3	9,650	2,100
5.....	75	141,000	75.4	16,250	1,610
6.....	74.5	118,000	48.6	21,200	2,090
7.....	75.0	91,000	21.0	38,000	3,750

by plotting the electrometer current against the electrostatic voltmeter reading under the conditions of frequency and pressures indicated in the legend. The intercepts of these curves with the voltage axis (or in the case of the curves with markedly asymptotic feet the intercepts of the extrapolated straight portions of the curves with the axis) yield the value of V_0 from which the mobility constant of the electron K is determined by the equation,

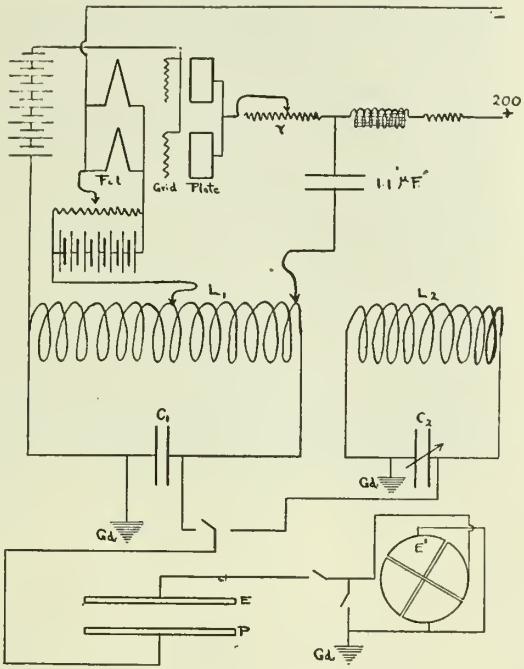
200
Fil
Grid
Plate
1.1 μF
L1
L2
C1
C2
Gd
Gd
Gd
E
P
E'

Fig. 1.

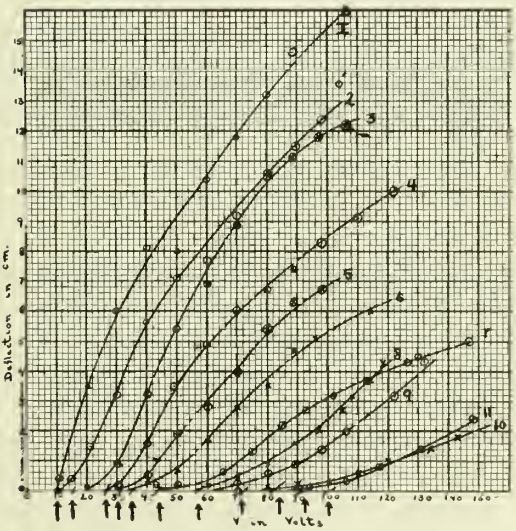
Deflection in cm.
V in Volts

Fig. 2.

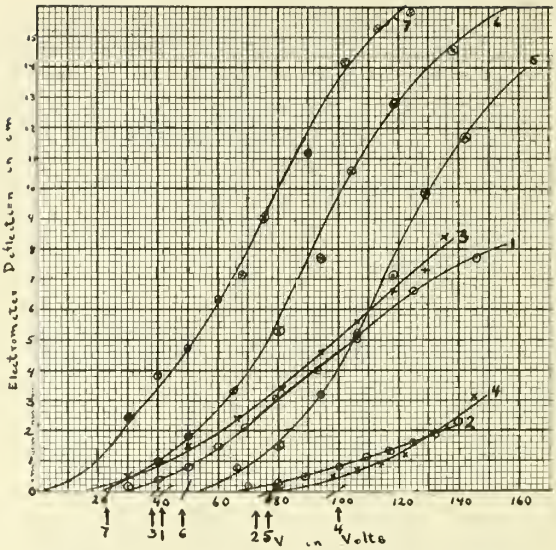

Fig. 3.

$$K = \frac{\pi n d^2 p}{\sqrt{2}\, V_0 760},$$

where n is the frequency of the oscillation, d is the distance between the plates PE, and p is the pressure in mm. of Hg. In this case as before the value of V_0 as obtained from the intercept must be corrected by a deduction of 4.6 per cent. of its value in the case where $d = 2$ cm. to take care of the drop in potential across the electrometer while the readings were being made. A discussion of the sources of error and the nature of the curves obtained will be postponed until a later point in the paper.

The mobility constants thus obtained were of the order of magnitude of 10,000 cm./sec. volt/cm. This is a value far in excess of any obtained by the previous investigators. It seems likely that the successful measurement of such high values was due to three essential differences between the writer's mode of procedure and those of the previous observers. All three of the workers mentioned above used electrons generated by the action of alpha particles on the gas in an auxiliary chamber (*i.e.*, they used the Franck modification of the Rutherford method), while the writer used photoelectrons freshly liberated from one of the plates. Furthermore the writer used extreme measures not only for purifying his nitrogen gas but also for reducing the contamination from the chamber to a minimum. That this was successful was shown by the fact that

nitrogen kept in the chamber for as long as 10 days still yielded electron mobilities which were of the same value as when the gas was freshly prepared. Finally the use of very high frequencies by the writer enabled only the purely electronic carriers to be studied. The other workers had used frequencies at most as high as 3,000 cycles per second, while the writer never used frequencies below 7,000 cycles and generally worked above 20,000 cycles. The mobility constants were furthermore found to vary through wide limits. It was found that by plotting K the mobility constant obtained from the equation above for a given value of d and p as a function of V_0, the voltage intercept, a smooth curve could in general be drawn through the points. For each value of d or p a

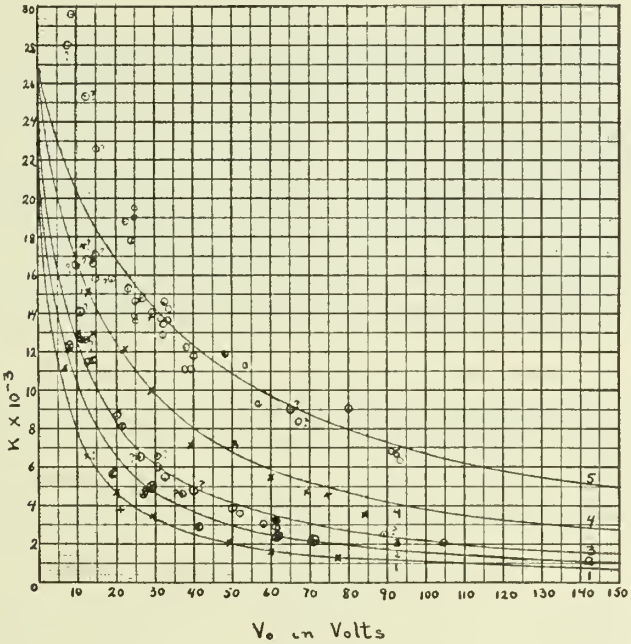

Fig. 4.

Mobility Constant K Plotted against V_0 Corrected.

No.	Press. p in Mm.	Plate Distance d in Cm.
1	75.5	2.00
2	160.0	2.00
3	304.0	2.00
4	150.0	1.52
5	606.0	2.00

different curve was obtained. The curves obtained for all the determinations are shown in Fig. 4. The legend gives the conditions under

which they were obtained. The curves were hyperbola of the form $K = a/(b + V)$. Furthermore if the equation for one curve with a given d' and p' be obtained (*i.e.*, that for curve (1) at $d = 2$ cm. and $p = 75$ mm. which is $K = 113/(4.18 + V)$) then it will be found that the equation for any of the other curves may be obtained from it, by multiplying the constants of this equation by $dp/d'p'$. Where d' and p' are the values of pressure and distance corresponding to the curve whose equation is known, and d and p are the pressure and distance corresponding to the curve to be determined. In other words, all the results may be expressed by means of the equation

$$K = \frac{571{,}000}{21 + (760V)/pd},$$

within the limits of error of the measurements. That this is the case is seen from the fit of the observed points to the curves plotted from the above formula. In noting this agreement it is well to point out that too much reliance must not be placed on the values of K obtained for intercepts at values of V_0 less than 10 volts. At this point owing to the extrapolation necessary to get the intercepts of the mobility curves, the values of K can easily vary as much as 30 per cent. or more. It is also interesting to note that as the pressures increase the deviations of the points on both sides of the theoretical curves become greater. This is in part due to the fact that a variation of say 10 per cent. from the curve at the higher values of the mobility will actually be greater in magnitude, than in the case where the mobilities are low.

The result obtained seems quite surprising and it is natural to inquire into the effects of possible sources of error before accepting them.

IV. Sources of Error.

(*a*) *Effect of Wave Form.*—The first question which arises is as to whether changes in the wave form of the oscillations due to higher harmonics might not influence the results. The equation given for the mobility for the case of an oscillation of pure sine-wave form was $K = 2.22nd^2/V_0$. For a square wave form, the equation becomes $K = 2nd^2/V_0$. The error introduced by a change from a sine-wave to a square wave, an extreme case, would be to give values of the mobility which are 11 per cent. too high. Errors due to neglect of wave form will therefore in general be slight.

(*b*) *How Does the Variation of K with V Affect the Mobility Curves and Hence these Determinations?*—One may next inquire as to the effect of the variation of the mobility constant K with the voltage on the

shape of the mobility curves. A theoretical study of the shape of the mobility curve for photoelectrons, liberated while the alternating field is acting, assuming a square wave form and that K is a constant yields the equation $I/I_0 = (V - V_0)/V$; where I is the current, I_0 is the maximum possible current, and V_0 is the critical value of the voltage when the electrons can just get to E. It has been found that for the case of the negative *ions*, where K is constant, such an equation reproduces the form of the observed mobility curves with a square wave fairly well. For the case of a sine-wave the equation for the electronic current as a function of the voltage for K constant is found to be $I/I_0 = 1/\pi \cos^{-1} \{(2 V_0/V) - 1\}$. The two types of curves for two different values of V_0 are shown in Fig. 5.

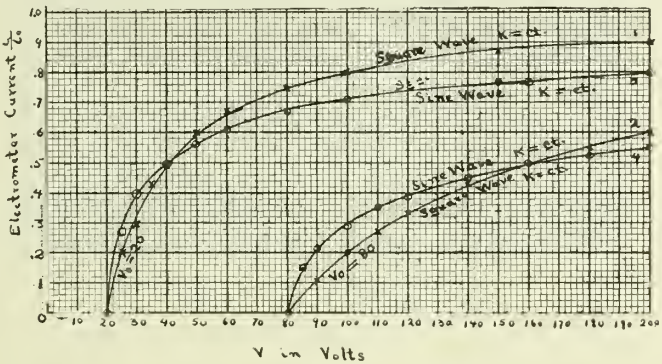

Fig. 5.

Theoretically computed curves for variation of current with an alternating voltage for ions or electrons for which the mobility constant K is constant. This is computed for photoelectrons.

No.	Wave Form.	V_0.
1	square	20.0
2	square	80.0
3	sine	20.0
4	sine	80.0

It is seen that they are similar in general form except that the curve for the sine-wave rises a bit more abruptly at first. If now K varies, as was found experimentally to be the case, viz., $K = a/(b + V)$, the equation for the square wave becomes one of the form,

$$I/I_0 = \left(1 - \frac{V_0 + V/b}{V}\right),$$

where $V_0 = nd^2/K_0$ and $K_0 = a/b$. On plotting this equation we get the types of curves seen in Fig. 6 for the positive values of the current.

The value of the intercept will if substituted in the mobility equation for a square wave form yield (*e.g.*, $K = 2nd^2/V_0$) values of K that vary as K was assumed to vary. For the case of the sine-wave with $K = a/(b + V)$ it is impossible to determine the equation directly. The mobility curves may, however, be determined for a given set of conditions, by means of graphic integration. This was done, and the curves so obtained for three values of V_0 are shown in Fig. 6. These curves are not unlike those obtained for the square wave form and differ from them chiefly in the sharper rise of the curve near V_0 and a slightly lower value of

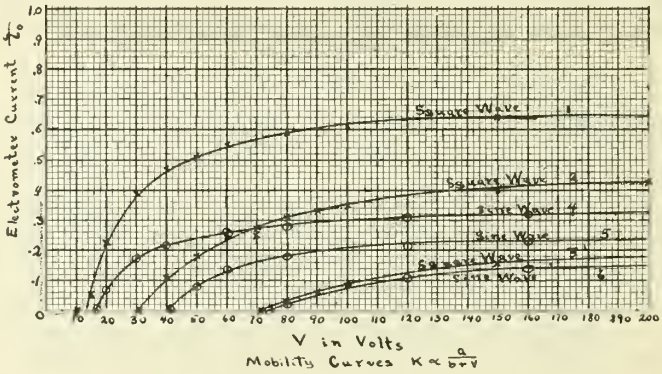

Fig. 6.

Theoretical curves for variation of current with an alternating voltage for electrons, for which K is a variable with V according to the equation, $K = a/(b + V)$. Values of the constants taken from experiment. Curves 1, 2 and 3 correspond to the curves for a square wave under the conditions of the experiment at frequencies of 30,000, 50,000 and 70,000 cycles and 606 mm. pressure. Curves 4, 5 and 6 correspond to the curves with a sine wave form and the same frequencies respectively at a pressure of 760 mm. The plate distance here is 2 cm.

i/i_0. It is at once seen that the apparent saturation values of the curves of Fig. 6 do not nearly rise to the values attained with K a constant (see Fig. 5). It is also to be noticed that these saturation values are progressively lower the greater the value of V_0. This peculiarity which had been observed in all the experimental curves (see Figs. 2 and 3), had puzzled the writer for some time, until it was found to be a natural consequence of the variation of K with voltage.

(*c*) *Discussion of the Asymptotic Feet of the Mobility Curves.*—There is another peculiarity of the curves which up to the present has not been satisfactorily explained. Since the electrons in crossing the plates make millions of collisions before they cross, it is to be expected that they all move with a nearly uniform velocity of drift in the direction of the field. Thus the intercepts of the mobility curves with the voltage axis should be quite sharp. Actually this is not the case. The mobility curves

have asymptotic feet which become more pronounced as the value of V_0 for the curves increases and so drags out these portions of the curves over a greater range of voltages. A study of these feet indicate that they are due to a factor which increases the electrometer current more and more rapidly as the quantity $V_0 - V$ decreases to 0. This portion of the curves is also apparently increased in importance by a decrease in pressure or a decrease in the distance between the plates. At present the only plausible explanation of these feet is that they are due to the formation of negative ions in the gas. Now the gas used, though quite pure, is not absolutely so. Therefore while the electrons are oscillating back and forth in the space between the plates some of them attach to form negative ions. These, owing to their low mobilities, remain between the plates. In the course of the million cycles which elapse while a measurement is being made this process might build up such a gradient of ions that some of these will diffuse to the upper plate E and register a current. The gradient built up will be the sharper (and hence the number diffusing will be the greater), the nearer the electrons get to crossing the distance between the plates, *i.e.*, the smaller $(V_0 - V)$, and the smaller the distance d. As a decrease in the pressure increases the coefficient of diffusion of the ions, it would also increase the number that get across. An attempt was made to remove these feet by putting a weak but constant field in the circuit in such a manner as to remove the accumulated ions as they were formed. The reduction in prominence of the feet produced by a field of .75 volt per cm. was however not sufficiently great to permit the explanation offered to account for the *whole* effect. It does however account for a portion of it.

(*d*) *A Possible Effect of the Unsymmetry of the Waves Relative to the Ground Potential.*—Finally one must consider the possibility that a state of affairs exists in the oscillating system such that the oscillations, that is the positive and negative crests of the waves, are unsymmetrically placed with respect to the ground potential. This condition, though unlikely in this type of circuit is, however, important enough when present to merit a brief discussion. Consideration will show that when the negative side of the wave has a higher peak value than the positive side, by even a small fraction, it will become impossible to obtain any mobility curves at all. For the electrons will be accelerated by the field for a longer time interval and by a greater average force when the phase is negative than when it is positive. Accordingly the electrons advance towards the electrometer plate E a distance d', and are pulled back from it a distance equal to d'', where $d' > d''$. Thus since the measurements last over a million or more cycles the electrons

get across the plates for very small potential differences. With the positive peaks higher than the negative peaks, the ions will cross as in the case for symmetrical waves. However, the value of V_0 taken from the curves, as registered on the static voltmeter, will be higher than the actual value of the driving potential. Also the time over which the potential acts will be shorter than that assumed from the frequency. The mobility as computed from readings under these conditions, will be lower than the actual value. If such an unsymmetry should actually occur and increase systematically with the increase in frequency, it might produce results analogous to those obtained. Calculation shows that to produce a mobility which is but 78 per cent. of the true value it requires that the height of the negative peak be .82 that of the positive peak. If the mobility were to be reduced to one fifth its true value the negative peak would have to be .33 as high as the positive peak. With a Braun tube oscillograph no unsymmetry of the oscillations over a considerable range of frequencies could be detected, within the limits of resolution of the oscillograph used. The instrument could easily have shown unsymmetry of .82 between the two peaks. Other tests also failed to reveal any unsymmetry. In no case was unsymmetry with the negative side greater than the positive side manifested by any mobility measurements. Finally the diversity of coils and the diversity of connections used in obtaining the oscillations should a priori have caused no systematic change of any unsymmetry present such as would be required to yield the results described.

V. The Interpretation of the Results on the Basis of Townsend's Electron Mobility Equation.

(*a*) *Modification of the Langevin Equation by Townsend.*—An interpretation of the variation of the mobility found is difficult. Townsend[6] suggests that the Langevin[7] equation for ionic mobilities may be applied to the case of electrons. In doing this one must assume that owing to the elastic impacts which the electron makes with the more massive molecules its energy of agitation in the gas (*i.e.*, its temperature), increases as it moves through the gas, due to the action of the field. Townsend[8] gives the Langevin equation, when it has been reduced to the case of a body of mass small compared with that of the molecules as

$$K = .815 \frac{e}{m} \frac{\lambda}{c}, \tag{1}$$

where e is the electronic charge, m its mass, λ its mean free path, and

[6] Townsend, J. S., "Electricity in Gases," Oxford, 1914, p. 174 ff; Phil. Mag., Vol. 40, 1920.

[7] Langevin, P., Ann. de Chimie et de Phys., 8, 5, p. 245, 1905.

[8] Townsend, J. S., Electricity in Gases, p. 180.

$\bar{c}$ its mean velocity of thermal agitation. This equation must be modified according to Townsend by multiplying the $\bar{c}$ by a quantity $\sqrt{k}$ before it may be applied to the case of the electron in an electric field. (A similar equation is given by Lenard[12] except that in his equation the constant term is .5 instead of .815 and that he uses α_1 in place of $\sqrt{k}$.) This quantity $\sqrt{k}$ must then be a quantity of such a form that when it is multiplied by c it gives the average velocity of agitation of the electron in the field. If the maximum energy which the electron can acquire due to the field alone be called W, the average energy of the electron as a result of the heat motions and the field must be given by $[2(m\bar{c}^2/2) + W]/2$. The average velocity of the electron as a result of thermal agitation and the action of the field will then become $\sqrt{\bar{c}^2 + W/m}$, and hence the quantity $\sqrt{k} = \sqrt{1 + W/m\bar{c}^2}$.

(*b*) *Consequences of This Equation for Elastic Impacts.*—Now the value of W will depend on how the electron gains and loses energy in the field. If, as is the case for the most part in helium and the monatomic gases, the impacts are nearly perfectly elastic, it will according to the quantum theory continue to gain in energy of agitation until it acquires enough energy to suffer an inelastic resonance impact. At the high pressures under which the experiments above were conducted the electrons probably exceeded their resonance potentials R very little before suffering a resonance impact. Also if the total fall of potential between the plates was several times that of the resonance potential, the value of W was probably close to $R \times e$, where e is the electronic charge. Thus the average velocity of the electrons in this case would approximate a value of the form $\bar{c}\sqrt{1 + Re/m\bar{c}^2}$. The mobility of the electron on Townsend's assumptions would then be given by

$$K = .815 \frac{e}{m} \frac{\lambda}{\bar{c}\sqrt{1 + \frac{Re}{m\bar{c}^2}}},$$

Since $Re/m\bar{c}^2 >> 1$,

$$K = .815 \frac{e}{m} \frac{\lambda}{\bar{c}\sqrt{\frac{Re}{m\bar{c}^2}}}.$$

It is seen at once that this mobility would be a constant depending solely on R, and would not vary as a function of p or d as was experimentally found to be the case.

(*c*) *Consequences of this Equation for the Case of Partially Elastic Impacts.*—Thus one must conclude that the electron in nitrogen does not

behave as in helium, but that it loses a fraction of its energy (f) at each impact. If this is the case Compton[12] has shown that the value of W for the electrons, after a sufficient number of impacts, approaches a terminal value given by

$$W = Ue = .575 \frac{Ve\lambda}{d\sqrt{f}},$$

which is in agreement with a result arrived at by Pidduck in a paper entitled "The Abnormal Energy of an Electron in a Gas."[11] Here V is the potential across the plates, d is the distance between them, and f is the fraction of the energy of the electron lost at each impact. The value of $\sqrt{k}$ then becomes

$$\sqrt{k} = \sqrt{1 + .575 \frac{Ve\lambda}{\sqrt{f}dm\bar{c}^2}},$$

and hence

$$K = .815 \frac{e}{m} \frac{\lambda}{\bar{c}\sqrt{1 + .575 \frac{Ve\lambda}{mdc^2\sqrt{f}}}}$$

on the basis of Townsend's reasoning. This of course only holds for the values of a terminal energy of agitation which is less than the resonance value Re discussed above. That such a fractional loss of energy (f) actually may occur in nitrogen gas is shown both by the results of Franck and Hertz,[9] and those of Compton.[10] The mobility of the electron in the equation above varies with the voltage, the distance between the plates, and with the pressure; for λ the mean free path varies with the pressure. The form of the variation of K with these quantities for the equation would however be

$$K = \frac{a}{\sqrt{1 + \frac{bV}{pd}}}$$

while the observed equation makes

$$K = \frac{a}{b + \frac{V}{pd}}.$$

The two equations, observed and theoretical, may only be caused to agree in case either $\sqrt{f}$, or λ, vary as a function of (V/pd). In the former case agreement can be had only if $\sqrt{f}$ increases as the value of V/pd decreases. That is when the loss of energy of the electron on impact

[9] Franck and Hertz, Verh. d. Deut. Phys. Ges., 15, p. 34, 1913; Verh. d. Deut. Phys. Ges., 15, p. 373, 1913.

[10] Compton, K. T., PHYS. REV., Vol. XI., 3, p. 196, March, 1918.

[11] Pidduck, F. B., Proc. Roy. Soc., A 88, p. 300, 1913.

[12] Lenard, P., Ann. der Phys., Vol. 40, p. 409, 1913.

decreases as the energy of the electron increases. It is well known that such a variation of the loss of energy of the electron occurs on impacts when the electrons move with high speeds. Whether such can be the case at the low values of the velocities of the electrons dealt with here is, however, doubtful.

(*d*) *Value of the Mean Free Path of Electrons in Nitrogen Deduced from the Results on the Basis of Townsend's Theory.*—Finally if in the general experimental equation for the mobility of the electron,

$$K = \frac{571{,}000}{21 + \frac{760V}{pd}},$$

the value of V be set equal to 0, it is seen that K becomes 27,200 cm./sec. volt/cm. On the Townsend point of view this represents the value of the mobility when the electron has a velocity equal to its velocity of thermal agitation in equilibrium with the gas molecules. The value of this mobility may be computed from the Townsend equation when V approaches 0, by setting the mean free path of the electrons as $4\sqrt{2}$ that of the nitrogen molecules. The value thus obtained is 6940 cm./sec. volt/cm. This marked difference in the two values may be interpreted as meaning one of two things. Either that one is not justified in applying the Langevin equation to the case of the electron at all, a point of view which may after all be correct; or that the mean free path of the electron is 3.9 times as great as that which has been assumed above.[13] If the latter view point is correct it is likely that the definition of the "mean free path" of an electron in a gas must be distinctly modified.

In conclusion the writer wishes to express his thanks to Prof. R. A. Millikan for his kind advice and criticism. The writer also desires to acknowledge his indebtedness to Dr. A. J. Dempster for many valuable suggestions and criticisms related to the more theoretical aspects of this paper.

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In applying these measurements to electrons in H_2 gas a new oscillating system was used in which the voltage V could be varied from 10–200 volts without changing the frequency. Measurements made on N_2 checked the values here given within the limits of experimental variation.—R. B. Loeb.

[13] This high value of the mean free path may have some justification in view of the recent results of Mayer and Ramsauer on argon at velocities of electrons below 3 volts. Ann. der Phys., Vol. 64, p. 451 and p. 613, 1921.

AN EXPERIMENT ON ELECTROMAGNETIC INDUCTION AND RELATIVE MOTION.[1]

By W. F. G. Swann.

Synopsis.

Electromagnetic Induction; Charging Effect of the Rotation of an Iron Sphere in a Uniform Magnetic Field.—The electromagnetic theory of this effect among others was developed by the author in a former paper. The answer which the theory gives is perfectly definite, but the nature of the problem is such that one who is accustomed to think in terms of moving lines of force may be uncertain as to the proper basis of attack and may even, quite plausibly, arrive at a result one third as great as it should be. Therefore *an experimental verification of the theoretical formula* seemed worth while carrying out. It was found that when an iron sphere with a radius of 3.17 cm. was rotated at rates ranging from 3,250 to 6,430 r.p.m., in a magnetic field ranging from 3,930 to 6,070 gauss, the changes of potential of an insulated copper shell surrounding the iron sphere, which were observed when the magnetic field was reversed ranged from 0.0114 to 0.0359 volt, while the corresponding calculated values ranged from 0.0116 to 0.0353 volt. In view of the experimental difficulties the fact that the average difference between observed and calculated changes of potentials for the seventeen sets of readings is only 1.7 per cent. is considered a satisfactory verification of the theory.

Introduction.

In a recent paper[2] the present author has discussed the so-called "Moving-line Theory" of electromagnetic induction, and has described the sense in which it must be interpreted in order to give the equivalent of the Maxwellian electromagnetic theory. It was shown, moreover, that, apart from effects of the order of magnitude of the ratio of the square of the velocity of a particle of matter to the square of the velocity of light, and concerned with the alteration of the constitution of the matter as a result of the motion, the electromagnetic theory contains a complete answer in the case of any problem concerned with the motion of magnets or of bodies in magnetic fields. There is no ambiguity such as frequently appears to present itself in discussions on moving lines of magnetic force, and concerned with whether the æther or the lines of magnetic force do or do not move with the bodies associated with them.

It appeared that if a symmetrical magnetized body were rotated about its axis of magnetization, the motion of the magnetized material would

[1] Presented at the meeting of the American Physical Society, December 28–30, 1920.

[2] Phys. Rev., Vol. 15, pp. 365–398, 1920.

give rise to an electric polarization perpendicular to the axis of rotation, in the case of a non-conductor; but, in the case of a conductor, the state of polarization would bring about a volume and surface distribution of charge which would completely annul the electric field at all external and internal points. At least this would be so in the absence of the "Motional Intensity" resulting from the motion of the substance of the conductor in its own magnetic field. This motional intensity results in the superposition of an electrostatic distribution upon the condition described above, and this electrostatic distribution is the sole representative of the ultimate effect as regards electric field. Moreover, not only is the electrostatic distribution produced by the motional intensity the sole representative of the ultimate electrical effect in the case of the rotation of a permanent magnet, but it is also the sole representative of this effect in the case of the rotation of a magnetizable body, or of course of a non-magnetizable body in an external field. In all cases the motional intensity is given by $[\mathbf{v}\cdot\mathbf{B}]/c$, where $\mathbf{v}$ is the velocity of the element of matter, c the velocity of light, and $\mathbf{B}$ the magnetic induction as measured by the force on a fixed unit magnetic pole placed in a thin drum-shaped cavity supposed cut out of the body, with its flat ends perpendicular to the flux.

In general, the electrostatic distribution resulting from the motional intensity results in a potential other than zero at the axis of rotation if this axis is insulated; and, in this case, moreover, the total charge associated with the electrostatic distribution is zero. If the axis of rotation is earthed, an additional charge comes to the body to bring the axis to zero potential, and it is of course possible to measure this charge.

In the paper above referred to, the present author has worked out the case for a sphere rotating in a uniform magnetic field, and has shown that, in the case where the direction of rotation is clockwise as viewed by an observer looking in the direction of the axis of magnetization, the potential produced at the axis of rotation when insulated is $-2\pi Bna^2/3c$ e.s.u., where B is the induction in e.m.u., n the frequency of rotation, a the radius of the sphere, and c the velocity of light. Under this condition, the total charge on the rotating sphere is zero, so that if this sphere were surrounded by an insulated sphere, the potential of the latter sphere would not be altered by stopping the rotation or reducing the magnetic field to zero; for, the various elements of charge on the inner sphere, which elements all add up to zero, would produce contributions to the potential of the outer sphere depending only upon their amounts, and independent of their positions. If we should now earth the axis, the inner sphere

would take a charge, and the potential of the outer sphere would alter by an amount V which we shall proceed to calculate. Our problem amounts to considering the simple electrostatic problem where the inner sphere is devoid of rotation and is initially at zero potential, and finding the potential V to which the outer sphere and its attachments rise when, without altering the total charge on them, we charge the inner sphere to potential $2\pi Bna^2/3c$; for, a superposition of this latter solution upon that corresponding to the case where the axis was insulated, the inner sphere was in rotation, and the outer sphere was at zero potential, obviously satisfies all the conditions of the problem.

If subscript unity refers to the inner sphere, and subscript two to the outer sphere and any attachments such as an electrometer, and if q_{22} and q_{12} refer to the usual coefficients of capacity and induction, we have, since the charge on the outer sphere and its attachments is zero as a whole:

$$q_{22}V + \frac{2\pi Bna^2}{3c} q_{12} = 0.$$

Hence[1]

$$V = -\frac{2\pi Bna^2}{3c}\frac{q_{12}}{q_{22}}. \tag{1}$$

The object of the present paper is to verify this result experimentally, and to this extent to verify the conclusions upon which it is based. To any one who takes his stand firmly on the basis of the Maxwellian theory, it would appear, in accordance with the discussion in the paper above referred to, that no reason exists for suspecting that (1) might be other than true. Presumably nobody would doubt its validity in the case of a non-magnetic sphere, one of copper for example, where there would be no temptation to raise considerations as to whether any part of the field took part in the rotation, and where the simple results of the motional intensity represent all that is to be anticpiated on any view of the matter. In the case of an iron sphere rotating in the field, however, it is quite conceivable that one who thought entirely in terms of moving lines might have some doubts as to the result, depending upon the manner in which he regarded the phenomenon.

[1] *Correction to previous paper.* The last step in the derivation of formula (23) is not quite correct, although the formula itself is correct. In the case of two concentric spheres of radii a and b, b being the larger, it is easy to show that $q_{12} = -ab/(b-a)$, and $q_{22} = b^2/(b-a)$. Thus, $q_{12}/q_{22} = -a/b$, which shows formula (23) of the previous paper to be in agreement with (1) above. In the case where the outer sphere is connected to an electrometer, b must be replaced by the measured capacity of the sphere and electrometer as stated in the paper, but one of the a's must also be replaced by $ab/(b-a)$, so that the resulting effect is to increase in the ratio $b/(b-a)$ the quantities 5×10^{-4} volt and 3×10^{-2} volt calculated on page 394.

Thus, for example, it is a well-known fact that if a sphere of large permeability (an iron sphere, for example) be placed in a uniform field of intensity H, the resultant field at all points is such as would be obtained by superposing upon the original field of intensity H, the field of a magnetized sphere of very approximately the following properties when considered as *isolated from the original field H.*

Intensity of magnetization of sphere $= I = 3H/4\pi$

Field intensity within sphere $= -H$

Induction B_1 within sphere $= -H + 4\pi I = -H + 3H = 2H.$

The superposition of the field of this sphere upon the original field H gives a resultant intensity zero, and a resultant induction $3H$, inside the sphere, while outside the sphere the field is that composed of the field intensity H together with the field intensity due to the magnetized sphere. Now one who thought in terms of moving lines of force might naturally be tempted to regard the portion of the field due to the magnetized sphere, *i.e.*, the part corresponding to an induction $2H$ within the sphere, as rotating with it, and consequently producing no effect, and the remaining portion H as stationary and so giving rise to motional intensity in the rotating sphere. Such a view would result in a value of V only one third of that given by (1). Slightly varied views as to

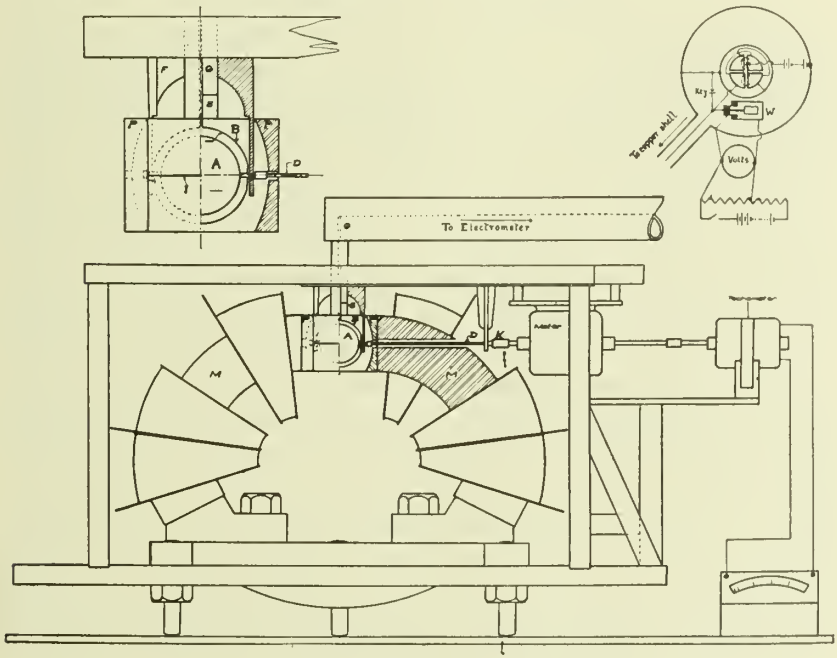

Fig. 1.

the phenomenon would lead to yet other conclusions. It would therefore seem that, at any rate from the point of view of a devotee of the moving line theory, something would be added to the conclusiveness of the arguments on which (1) is based by an experimental verification of that formula.

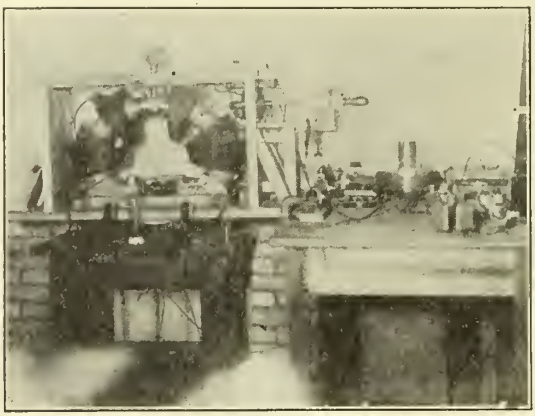

Fig. 2.

Experimental Procedure.

General Description of Apparatus.—The apparatus is represented diagrammatically in Fig. 1, which is drawn to scale, and a photograph of the apparatus, exclusive of the electrometer system, is shown in Fig. 2. The iron sphere, and the parts immediately associated with it, were mounted between the poles of a large electromagnet *MM*. The sphere was driven through the shaft *D* by a high-speed motor, whose axle was connected at one end to a Hopkins electric tachometer, for the purpose of registering the speed of rotation. The pole pieces *PP* were specially formed so as to give a uniform induction within the sphere, in accordance with the tests to be described later. The rotating sphere *A* was surrounded by a thin copper shell *B*, made in two halves, and supported by a rod *G* passing through a sulphur plug *S*, and connected to a Dolezalek electrometer as indicated. All parts of the insulated system were of course carefully inclosed in shields which were connected together electrically; and, the insulated shell itself was boxed in by a cylindrical zinc cover fastened to the brass frame *F* which supported the axle bearings. The bearings were of brass, and were very carefully made, on account of the high speed of rotation used. They were finally ground with rouge until the necessary perfection of fit was obtained, and were lubricated

[1] Thomson, J. J., Phil. Mag., Sept., 1915.

frequently while in use. The various parts concerned in the support of the sphere system, shaft, and motor, were mounted on a single stone slab for steadiness, and this slab was fitted into the solid wooden frame which supported the electromagnet, in the manner shown.

It was anticipated that charging of the copper shell might result from mere rotation of the iron sphere without magnetic field, as a consequence of friction with dust in the air. The inside of the copper shell was consequently smeared with vaseline, so as to insure that dust which struck it would stick, and in this way it was hoped that any undesirable effects of the kind anticipated would be quickly eliminated during the rotation of the sphere. That such effects were reduced to a sufficiently satisfactory minimum is borne out by the observations described below.

Contrary to expectation, it was found that the induction produced in the sphere by excitation of the electromagnet was always the same for a given exciting current in the coils, at least to the degree of accuracy with which the Grassot fluxmeter used would record. This was a matter of great convenience, because it enabled the fluxes to be determined once for all, for the various exciting currents used, so that all that was necessary in the main experiments was a measurement of the exciting current in the electromagnet. The flux, for the various exciting currents used, was measured by winding four turns of No. 36 double silk covered wire around that great circle of the iron sphere which was perpendicular to the axis of rotation, the leads from the coil being of course twisted together, and then taking the throw on the Grassot fluxmeter when the current was switched on, and when it was switched off. Considerable attention was given to the uniformity of the flux, a matter which will be discussed in detail later.

The electrometer system is shown at the top of Fig. 1, to the right, and is largely self-explanatory. The original intention was to measure the charge which it was necessary to give to the insulated shell to keep it at zero potential after the magnetic field had been applied to the rotating iron sphere; and, to this end, the insulated quadrant was connected to a small condenser W, whose outer member was connected to the sliding member of a rotary potentiometer, the potential applied being measured by a voltmeter. It was later found more convenient to read electrometer deflections; but, the condenser and potentiometer served a convenient purpose in determining the ratio q_{12}/q_{22}, and they were also of use in checking up the electrometer sensitivity at any time. For, if the factor to reduce electrometer deflection to volts be denoted by k, which is supposed determined by applying a known potential to the quadrant, if β is the deflection produced by raising the outer member of the con-

denser W from zero to U, and Q_{21} the coefficient of induction between the outer member in question and the insulated system, we have:

$$q_{22}k\beta + Q_{21}U = 0. \tag{2}$$

If on some future occasion, when k has changed slightly for some reason or other, we measure the corresponding values β_1 and U_1 of β and U, we have:

$$\frac{k_1}{k} = \frac{U_1\beta}{U\beta_1}, \tag{3}$$

which serves to determine k_1 in terms of k. Of course there is no special advantage in this method of checking up on the variations of k over that involved in measuring k itself on each occasion except that, the condenser W being part of the apparatus, no additional connections were necessary to enable a test to be made at any time.

General Procedure in the Main Experiments.—The sphere was set in rotation with an exciting current of 8 amperes in the electromagnet, and the speed of rotation was adjusted by an assistant to about 3,300 r.p.m., and kept there as steadily as possible, by means of a rheostat in the motor circuit. The same assistant also watched the electromagnet ammeter, and kept its reading at 8 amperes. When the conditions of speed had become steady, and under satisfactory control, the electrometer quadrant was released from earth. After any momentary fluctuations of the electrometer spot had subsided, and the reading was about to be taken, warning was given to the assistant, who then took special pains to keep the speed steady. A second or two later, the electrometer reading θ_1 was taken, and, at the same instant, the assistant recorded the speed, and ammeter reading. The current through the electromagnet was then reversed by means of a switch, while the sphere was kept in rotation. As a result, the electrometer showed a deflection. The assistant adjusted the electromagnet current and the speed to as nearly as possible the same values as before; and, when the electrometer spot had come to rest, he was again warned to prepare to read the ammeter and tachometer when the signal was given. A few seconds later, the electrometer reading θ_2 was taken, the assistant reading the speed and ammeter at the same instant. The current through the electromagnet was reversed once more, and readings corresponding to the first set were taken. The whole experiment was carried out, in the above manner, four times. The procedure was then repeated for exciting currents of 10, 12, and 16 amperes in the electromagnet. Finally, the whole series of observations for the different exciting currents was gone through again for speeds of rotation of 4,800 r.p.m. and 6,400 r.p.m.

In each of the above sets of observations, the agreement of the first and last electrometer readings θ_1 and θ_3 gave a good check on any possible charging effect which had resulted from causes other than that under investigation. The difference between θ_1 and θ_3, regardless of sign, and expressed as a percentage of the change of deflection on reversal of the magnetic field amounted, on the average, to 4.2 per cent. To the extent that the small spurious charging effect was uniform during the three readings, it of course became eliminated on taking the mean of $\theta_2 - \theta_1$ and $\theta_2 - \theta_3$; and, the potential change ΔV corresponding to this mean, since it is the change of *reversal* of the magnetic field, corresponds to twice the value of V given by (1), so that the theoretical formula for ΔV is:[1]

$$\Delta V = -\frac{4\pi Bna^2}{3c}\frac{q_{12}}{q_{22}}. \tag{4}$$

A check on the sensitivity of the electrometer was made at the end of each day's observations, so that all that was necessary to complete the test of (4) was a determination of q_{12}/q_{22}.

Determination of q_{12}/q_{22}, and Electrometer Sensitivity.—We have seen (equation 2) that if β is the electrometer deflection resulting from the application of a potential U to the outer member of the condenser W,

$$q_{22}k\beta + Q_{21}U = 0.$$

If now we earth the outer member of W, insulate the iron sphere temporarily from its shaft and bearings, and, by means of a potentiometer, alter its potential from zero to v, the quadrant having been earthed and then insulated just before applying the potential v, we shall obtain a deflection of the electrometer. If u is the amount by which it is necessary to alter the potential of the outer member of W in order to compensate this deflection, we have:

$$q_{12}v + Q_{21}u = 0,$$

which, in combination with the previous equation, leads to:

$$\frac{q_{12}}{q_{22}} = \frac{k\beta u}{Uv}, \tag{5}$$

so that the determination of q_{12}/q_{22} does not involve a knowledge of the absolute value of Q_{21}. In carrying out the second of the above experiments, the iron sphere was insulated from its bearings by a layer of paper.

[1] The fact that the earthed axle has a finite cross section and is not a geometrical line only produces an error of the order 0.5 per cent. in these experiments.

Corresponding to a value $U = 4.5$ volts, the value $\beta = 27.4$ divisions was obtained as a mean of three results with a maximum difference of one per cent. A simultaneous measurement of k gave $k = 1{,}226 \times 10^{-3}$ as a result of three determinations differing by less than one half of one per cent. As a mean of five almost identical determinations, the value 5.76 volts was found as the value of u necessary to compensate the potential $v = -0.333$ volt applied to the iron sphere, so that, inserting these values in (5), we obtain:

$$\frac{q_{12}}{q_{22}} = -0.1290.$$

Inserting this value in (4), together with the values 3.17 cms. for the radius of the iron sphere, and 3.00×10^{10} cm./sec. for the velocity of light, and introducing, moreover, a factor 1/60, so that in the resulting formula, n may be expressed in r.p.m., we have, for the theoretical value V of the change of potential of the shell as a result of reversing the magnetic field:

$$\Delta V = 0.906Bn \times 10^{-9} \text{ volt.} \tag{6}$$

The final experiments were made on December 2, 4 and 6, 1920, and the values of k, determined in the manner described from the standard value $k = 1.226 \times 10^{-3}$ are respectively: 1.178×10^{-3}, 1.226×10^{-3} and 1.234×10^{-3} volt per millimeter.

Subsidiary Considerations.

Calculation of Mean Speed and Deflection.—As explained above, each experiment under any one set of conditions involves the observation of three electrometer readings, θ_1, θ_2, and θ_3, and three corresponding, but slightly differing speeds of rotation s_1, s_2, s_3. It might appear at first sight that the proper procedure in averaging the results would be to calculate $\Delta\theta = (\theta_2 - \theta_1 + \theta_2 - \theta_3)/2$ and take this as corresponding to the speed $(s_1 + s_2 + s_3)/3$. Such a procedure is not quite exact, however, for the reading θ_2 figures twice in the calculation of $\Delta\theta$, so that s_2 should be given more weight than would correspond to the above method. In fact, the matter may be regarded in the following light: If θ_0 is the true zero of the electrometer, we may write:

$$\theta_2 - \theta_1 + \theta_2 - \theta_3 = (\theta_0 - \theta_1) + (\theta_2 - \theta_0) + (\theta_2 - \theta_0) + (\theta_0 - \theta_3),$$

which shows that the mean value of $\Delta\theta$, calculated as above, is equivalent to that which would have been obtained if the mean of four readings of $\Delta\theta/2$ had been obtained, each one measured from the true zero of the electrometer, and the result had then been doubled. It is therefore

obvious that the appropriate mean speed to combine with the above mean value of $\Delta\theta$ is $(s_1 + s_2 + s_2 + s_3)/4$. In the results given in the final tables, the mean speeds have been calculated in this way.

The Uniformity of the Magnetic Induction, and the Calculation of B for the Final Experiments.—A sphere made from the same piece of iron as the main sphere, and of exactly the same size, was used for the tests on uniformity of the field. It was coated with wax; and, after it had been mounted on a lathe, three grooves were cut in the wax, one along a great circle, and the others along small circles parallel to the great circle. Coils of fine wire were wound in these grooves, and a fourth coil was wound around the axle. It was by comparing the throws obtained in the fluxmeter from these various coils when the magnetic field was turned off and on that the uniformity of the induction was investigated. We shall denote by subscripts 1, 2, 3, 4, the various coils, including the axle, subscript unity referring to the largest coil. In addition, we shall use the following symbols, with their appropriate subscripts, to designate the quantities indicated:

B—Average corrected [1] flux per sq. cm. through a coil.

N—Number of turns on coil ($N_1 = 4$, $N_2 = 6$, $N_3 = 20$, $N_4 = 20$).

S—Effective area of coil [1] ($S_1 = 31.9$, $S_2 = 21.05$, $S_3 = 6.70$ sq. cm.).

φ—Throw obtained in fluxmeter on turning on some definite current in the electromagnet.

α—Ratio of cross-sectional area of axle to that of coil. (The cross-sectional area of the axle was 0.173 sq. cm., and $\alpha_1 = 0.0054$, $\alpha_2 = 0.0082$, $\alpha_3 = 0.0252$.)

G—Constant for converting fluxmeter throws to e.m.u.

The fluxes through the various coils are then given by:

$$B_1S_1 = G\left(\frac{\varphi_1}{N_1} - \frac{\varphi_4}{N_4} + \alpha_1\frac{\varphi_1}{N_1}\right), \tag{7}$$

$$B_2S_2 = G\left(\frac{\varphi_2}{N_2} - \frac{\varphi_4}{N_4} + \alpha_2\frac{\varphi_2}{N_2}\right), \tag{8}$$

$$B_3S_3 = G\left(\frac{\varphi_3}{N_3} - \frac{\varphi_4}{N_4} + \alpha_3\frac{\varphi_3}{N_3}\right). \tag{9}$$

[1] Since the lines of induction enter the sphere practically normally, the area concerned is not the true mean area of the coil, but the mean area of the coil projection marked out on the sphere by dropping thereon perpendiculars from all points of the coil. The correction only amounted to one half of one per cent. for the thin wire used, except in the case of coil 3, where the employment of 20 turns of wire necessitated having more than one layer. In the case of this coil, the correction amounted to 2 per cent. The uncorrected areas were obtained by measuring the lengths of wire with which the various coils were wound.

Each side of one of these equations represents, of course, the average total flux through one turn of the corresponding coil.

These formulæ need some explanation. Taking the first formula, for example, the true average flux through one turn of the coil in question would be $G\varphi_1/N_1$. The axle contributes an unfair share to this flux, however, in view of the fact that it projects beyond the sphere, and so affords a particularly easy path through itself for the magnetic lines. Moreover, this excess flux through the axle contributes practically nothing to the effect in the main experiment, since it exists through a part of the sphere where the linear velocity of the material is practically zero. To allow it to contribute to the calculated flux would be equivalent to supposing that its effect was the same as if it were distributed uniformly throughout the sphere, whereas, its effect is quite negligible compared with what it would be were it so distributed. It is therefore desirable to omit, from the total flux, the excess contributed by the axle. If we subtract $G\varphi_4/N_4$ from $G\varphi_1/N_1$ we omit not the excess, but the whole flux through the axle, so that the result so obtained must be again corrected by the addition of $G\alpha_1\varphi_1/N_1$. Such then is the explanation of equations (7), (8), and (9). When it is observed that, in the case of the large coil, for example, the second two terms on the right-hand side of (7) form only about three per cent. of the first term, we see that the above method of procedure is quite justified.

Tests of the uniformity of the flux, *i.e.*, of the equality of B_1, B_2, and B_3 were made with currents of 8, 10, 12, and 16 amperes in the electromagnet coils. With flat poles, a very considerable lack of uniformity existed, and it was thought that the best results would be secured by mounting the iron sphere and its surrounding copper shell in a hole cut out of a cylinder of iron, which cylinder was fixed to the support F (Fig. 1), and fitted between the poles of the magnet. With this arrangement the effect is the same as if the magnetic circuit of the electromagnet were completed by iron, except for the spherical hole in which the copper shell and the iron sphere are mounted. Unfortunately, this plan was quite unsuccessful; nor was it possible, by pulling the poles away from the iron cylinder and inserting pieces of iron of various shapes, to improve the uniformity of the field to the desired extent. Finally, the iron cylinder was discarded, and the iron sphere, with its copper shell and zinc outer cover, were mounted directly between the poles of the electromagnet, the latter being cupped to the shape which gave the best results. With this arrangement, the following set of values was obtained for the flux per square centimeter through the various coils, with the electromagnet currents indicated:

TABLE I.

Showing Uniformity of Flux in Sphere.

Current in Magnet Amperes.	Flux per Sq. Cm. of Coil in E.M.U.		
	B_1.	B_2.	B_3.
8	3,980	4,030	3,760
10	4,660	4,720	4,470
12	5,190	5,260	5,020
16	6,120	6,250	6,010

The above numbers represent calculations, based on equations (7)–(9), from the mean of two sets of observations, each set being obtained by observing the mean of the fluxmeter throws on starting and stopping the current in the electromagnet. No two observations in corresponding sets differed by more than one per cent.; and, the agreement was, on the average, good to one half of one per cent. It must of course be borne in mind that the uncertainty of the results in the main experiments is less than the divergence from uniformity shown by Table I. For, although the average value of the flux per square centimeter through a great circle was used in the calculation of the final result, lack of uniformity of the field only introduces error to the extent that a transference of a portion of the flux from one part of a cross section to another does not leave the electromagnetic effect unchanged in view of the greater efficacy of the flux in the regions of larger radius, resulting from the greater velocity there. The comparatively good agreement between the values of B_1 and B_2, moreover, presents a very satisfactory feature, since it implies that the flux per square centimeter in the outer and more important regions of the sphere is closely equal to the *average* flux per square centimeter taken over a cross section of the great circle.

The calculation of the average flux per square centimeter through the great circle of the main sphere was not made on the basis of the above observations, but on the basis of observations made on the main sphere itself. As already stated, the observations consisted in measuring the throws obtained from a coil of four turns wound around the great circle. The effective area to use in the calculation of the flux per square centimeter is the area of the great circle, and not the mean area of the coil, since the field intensity just outside the sphere at the equator is sensibly zero. The difference between the two areas is of course extremely small. The values of B, obtained on the basis of equation (7), from two sets of observations in which no two determinations differed by more than one part in three hundred are: 6,070, 5,130, 4,610, and 3,930 e.m.u. for exciting currents of 16, 12, 10, and 8 amperes respectively.

THE FINAL RESULTS.

The complete sets of observations are too lengthy to print; and, it will suffice to give the condensed digest of the results shown in Table II.

TABLE II.

Abridged Table of Final Results for an Iron Sphere 3.17 Cms. in Radius.

Date.	No. of Obsns.	Speed R.P.M.	B E.M.U.	V (Volts $\times 10^{-2}$) Observed.	V (Volts $\times 10^{-2}$) Calculated.	Diff. Per Cent.
Dec. 2....	4	3,280	3,930	1.18	1.17	− 0.8
	4	3,450	4,610	1.44	1.44	0.0
	4	3,260	5,130	1.53	1.51	− 1.4
	5	3,250	6,070	1.73	1.79	+ 3.5
Dec. 4....	4	3,250	3,930	1.14	1.16	+ 1.8
	4	3,290	4,610	1.37	1.37	0.0
	4	3,300	5,130	1.54	1.53	− 0.7
	4	3,250	6,070	1.84	1.79	− 2.8
	4	4,830	3,930	1.80	1.72	− 4.4
	4	4,840	4,610	2.05	2.02	− 1.5
	4	4,850	5,130	2.28	2.25	− 1.3
	4	4,900	6,070	2.67	2.69	+ 0.7
	2	5,600	6,070	3.10	3.08	− 0.7
Dec. 6....	4	6,430	3,930	2.36	2.29	− 3.0
	5	6,460	4,610	2.78	2.70	− 2.9
	4	6,430	5,130	3.06	2.99	− 2.3
	4	6,430	6,070	3.59	3.53	− 1.7

The numbers in the second column indicate the numbers of sets of observations for which the data given represent the means. Thus, for example, the last line represents four observations in which the speeds were 6464, 6408, 6424, and 6432 r.p.m., giving the mean 6430 r.p.m., expressed to three figures, while the corresponding observed values of ΔV were 3.54, 3.60, 3.63, and 3.58 hundredths of a volt, giving the mean 3.59 hundredths of a volt. Moreover, each of these individual observations corresponds to three measurements of speed, and three readings of the electrometer, as explained above under "General Procedure in the Main Experiments." As stated, moreover, under that section, the discrepancy between the first and third readings of the electrometer was, on the average, only 4.2 per cent. of the change of deflection on reversal of the magnetic field; and, even this small amount became eliminated by the method of taking the observations. As an additional precaution, tests were made to ascertain whether any electrometer deflection was

produced by merely turning on the magnetic field in the absence of any rotation of the sphere; but, neither with the smallest nor with the largest field used was any vestige of such an effect observed. It is hardly necessary to add that the *sign* of the observed effect is in accordance with the theory, and corresponds to an increase in potential of the shell as a result of superposing a magnetic induction in such a direction that, as one looks in that direction, the direction of rotation of the sphere is clockwise.

The greatest difference shown by Table II., between the calculated and observed values of ΔV amounts to 4.4 per cent., and the average percentage difference, estimated regardless of sign, amounts to only 1.7 per cent.; so that, in view of the comparative smallness of the quantities measured, and of the rather exceptional conditions attending the employment of high speeds of rotation, and fairly large magnetic fields, the observations may be taken as a satisfactory verification of the theoretical formula.

The expenses of the above investigation have been, in part, defrayed by a grant made by the executive committee of the graduate school of the University of Minnesota. The writer desires to take this opportunity of expressing his sincere thanks to the committee. He also wishes to express his appreciation of the services rendered by his research assistants, Mr. W. B. Haliday, and Mr. D. Hartwell, and by the laboratory mechanician, Mr. C. Dane.

Department of Physics,
University of Minnesota,
August 29, 1921.

A NEW TONE GENERATOR.

By C. W. Hewlett.

Synopsis.

New Pure Tone Generator and Receiver of Sounds.—(1) *Construction and operation.* The instrument consists of a thin, non-magnetic, metallic diaphragm between two flat coils through which a constant direct current I_0 flows in such a way as to produce a radial magnetic field in the diaphragm; then when a simple harmonic alternating current I of the frequency $\omega/2\pi$ is superposed upon the direct current, circular currents are induced in the diaphragm, which thereupon is acted upon by a simple harmonic electrodynamic force and vibrates with the frequency of the alternating current. For low frequencies the electrodynamic force is approximately proportional to $\omega I_0 I \sin(\omega t + \theta)$ and the amplitude of vibration is approximately proportional to $I_0 I/\omega$. The absence of overtones is due to the absence of ferromagnetic material, and to the fact that the radial magnetic field is constant. The aperiodicity of the diaphragm renders the calculation of the performance of the instrument practicable, and eliminates distorsion, due to resonance, in the wave form of the emitted sound when the instrument is excited by a complex alternating current. When used as a generator of pure tones, the coils were connected in the circuit of a thermionic oscillator whose frequency could be varied from 500 to 25,000 vibrations per second. When used as a receiver of sound, the current generated in the coils by the motion of the diaphragm is fed into a thermionic amplifier. (2) *Quantitative study of the performance.* The distribution of the magnetic field between the coils was determined experimentally; the diaphragm current equations were deduced and solved for a particular case; the forces on various parts of the diaphragm were calculated, and thence the amplitude of vibration and the sound energy output. With an aluminum diaphragm 0.0025 cm. thick and 10 cm. in diameter, a direct current of 1 ampere, an alternating current of 0.085 ampere, and a frequency of $10^5/2\pi$, these were respectively 7×10^{-7} cm., and 9 ergs per second. By increasing both direct and alternating currents five-fold, the output could be increased over six hundred-fold. Measurements of the amplitude for various frqeuencies agreed well with the calculated values. (3) *Applications of the instrument.* Since it gives a pure tone of constant and measurable pitch and intensity over a wide range, it would serve as a *precision source of sound*, useful both for research and lecture purposes. When used as a *telephone receiver and transmitter*, actual tests have shown that the reproduction of sound is remarkably faithful.

Introduction.

In a previous publication[1] the author gave a brief description of a new instrument for generating simple harmonic sound waves. The following is a quantitative description and study of the instrument and its performance, together with a discussion of some of its applications.

[1] Phys. Rev., 17, p. 257, 1921.

I. Specifications for the Construction of the Tone Generator, and Description of a Method of Operation.

The instrument described below was used successfully at frequencies from 500 to 25,000 vib./sec. For lower frequencies the instrument should be wound with a larger number of turns, while for higher frequencies a smaller number of turns of coarser wire should be used.

Figure 1 is a section and elevation. The frame is made of hard fiber,

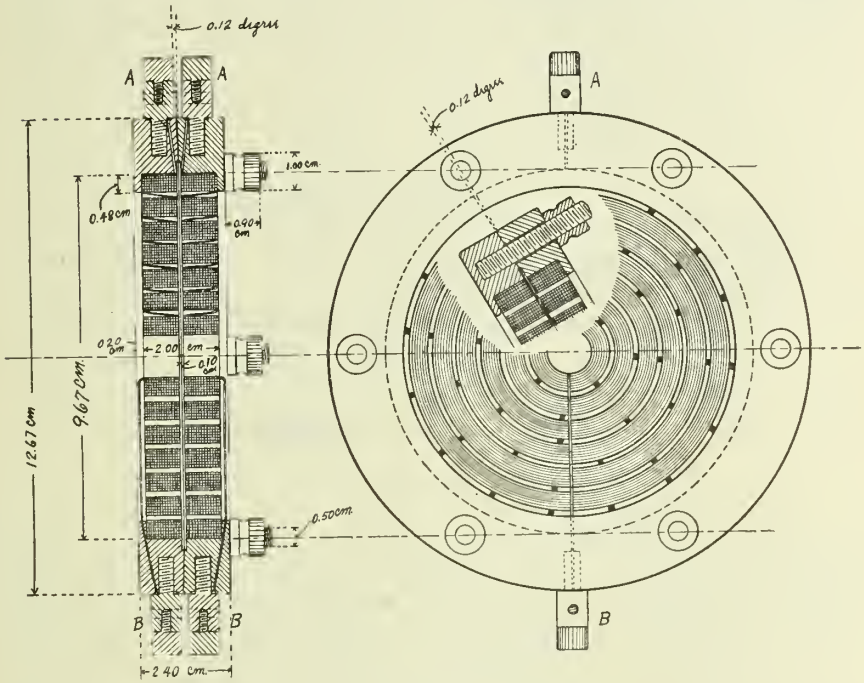

Fig. 1.

and the clamps and binding posts of brass. Each section of the pancake coils contains 98 turns of No. 22 wire, wound in 7 layers. The inside diameter of the innermost section is 1.11 cm., while that of the others is obtained by adding 1.27 cm. successively. These sections were wound on forms, shellaced, baked, and then bound at intervals with silk threads (not shown in figure). The sections mounted concentrically, are held in position by hard wood plugs. The sections of each coil are connected so that the direction of winding is continuous. The frame was turned after completing the coils, and the latter were glued in place with shellac. The taper on the clamping surfaces stretches the diaphragm enough to prevent appreciable sagging.

Any kind of metallic diaphragm will work; the author uses sheet aluminum 0.0025 cm. in thickness. Of the non-magnetic metals, alumi-

num gives the best results. An iron diaphragm gives more intense sounds at low frequencies for a given electrical input, although it will not emit a pure tone even when the instrument is excited by a simple harmonic alternating current. The diaphragm should be thin, as increasing the thickness decreases the intensity of sound emitted for a given electrical input, particularly for high frequencies. The reasons for the above may be drawn from the quantitative discussion of the performance of the instrument.

Figure 2 shows a method of using the instrument. The inductance

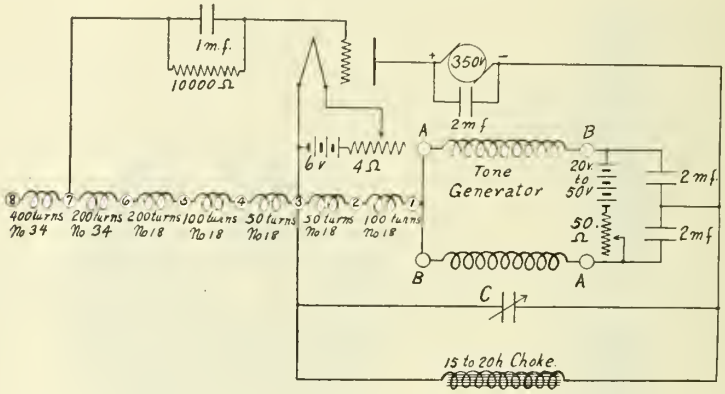

Fig. 2.

with the binding posts 1 to 8, is wound on a wooden core 20 cm. in diameter, and 6.5 cm. long. Coil 1 to 2 is innermost, and the others follow in numerical order. The wire is double cotton covered, and the layers are separated by friction tape. The best conditions for oscillation at any frequency can be obtained by adjustment of grid and filament connections to this inductance. In the actual circuit, *C*, and the choke coil are connected directly to the filament, and a single wire leads from this point to the inductance. The choke coil is home made. *C* consists of two 1 m.f. divided mica condensers, and five oil-filled rotary condensers whose combined maximum capacity is a little greater than the smallest step obtainable with the mica condensers. The other condensers are telephone condensers. The generator may be replaced by a battery, in which case no by-pass condenser is needed. The voltage shown is suitable for the Western Electric 205 B tube. The intensity of the sound from the instrument is controlled by the rheostat in series with the battery furnishing the polarizing current. The frequency of oscillation was measured with an improvised wave meter using a vacuum thermocouple for indicating resonance. If desired the instrument may be operated from a separate generator.

II. Quantitative Investigation of the Performance of the Instrument.

1. *Determination of the Distribution of the Magnetic Field in the Space occupied by the Diaphragm between the Pancake Coils.*—To simplify matters, the field of only one of the coils was investigated. Obviously the field is symmetrical about the coil axis. A flat spiral, of pitch 0.084 cm., consisting of 54 turns of No. 36 wire was wound in a shallow groove on the face of a fiber disc 10 cm. in diameter.

The spiral was connected to a ballistic galvanometer and a known current was established in the coil. The galvanometer deflection was determined for reversal of this current, (*a*) with the spiral and coil coaxially in contact, (*b*) when 1 mm. apart. The outside turns of the spiral were removed two at a time, making the above determinations after each removal, until only two turns remained. These determinations together with a calibration of the galvanometer yielded the necessary data for calculating the normal and radial components of the magnetic induction near the coil face. To simplify the calculation each spiral turn was assumed equivalent to a circular turn whose diameter is the mean diameter of the spiral turn.

Curve I., Fig. 3, shows the normal component of the magnetic induc-

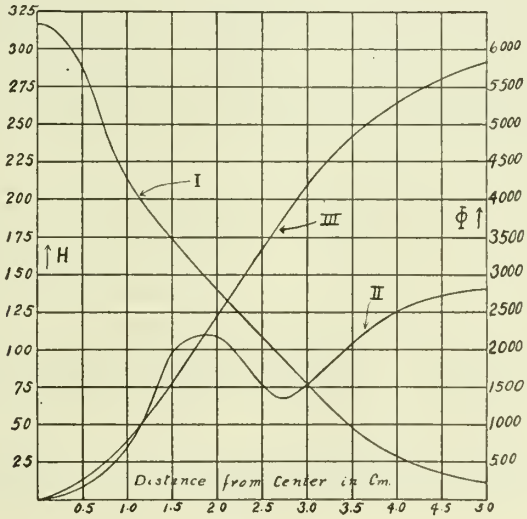

Fig. 3.

tion in C.G.S. units, as a function of the distance from the center, in the space between the two coils, when the latter are separated by a distance of 1 mm., and each carries a current of 1 ampere, their polarity being so adjusted that the unlike faces of the coils are adjacent. In this case

there is no radial component of the magnetic induction in the space between the two coils. Curve III. shows the total flux through a coaxial circle between the two coils as a function of the radius of the circle, for the same conditions of relative positions of the coils, current, and polarity as specified above. Curve II. shows the distribution of the radial component of the magnetic induction when the coils are separated by a distance of 1 mm., and each carries a current of 1 ampere, their polarity being so adjusted that the like faces of the coils are adjacent. In this case there is no normal component in the space between the two coils.

2. *Calculation of the Current Induced in, and Electromagnetic Forces Acting on the Diaphragm.*—The current in the diaphragm will flow in circles coaxial with the coils. The path of each current element will have a different resistance and self inductance, a different mutual inductance with the other paths, and will be acted upon by a different induced e.m.f. The current density and phase will therefore vary from one path to the next. The diaphragm was regarded as 8 annular rings each having a width of 0.645 cm., their mean diameters ranging from 0.97 cm. to 10 cm. Each annulus was considered equivalent to a circular wire of circular cross section of the same mass, material and diameter.

Suppose the current in the coils is given by $I_0 \sin \omega t$. The maximum values of the magnetic flux through each annulus was determined from curve III., and from these were calculated the induced e.m.f.'s in the annuli owing to the current in the coils. The total rise of potential around each annulus was then equated to 0, and the resulting eight equations put in the following form:

$$\left.\begin{array}{l}
\left(\frac{r_1}{\omega^2} + a_{11}\right) i_1 + a_{12} i_2 + a_{13} i_3 + \cdots + a_{18} i_8 = b_1 \sin \omega t + \frac{\Phi_1}{\omega} \cos \omega t \\
a_{21} i_1 + \left(\frac{r_2}{\omega^2} + a_{22}\right) i_2 + a_{23} i_3 + \cdots + a_{28} i_8 = b_2 \sin \omega t + \frac{\Phi_2}{\omega} \cos \omega t \\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
a_{81} i_1 + a_{82} i_2 + a_{83} i_3 + \cdots + \left(\frac{r_8}{\omega^2} + a_{88}\right) i_8 = b_8 \sin \omega t + \frac{\Phi_8}{\omega} \cos \omega t
\end{array}\right\},$$

where

$$a_{nm} = \frac{M_{n1} M_{1m}}{r_1} + \frac{M_{n2} M_{2m}}{r_2} + \frac{M_{n3} M_{3m}}{r_3} + \cdots + \frac{M_{n8} M_{8m}}{r_8}$$

and

$$b_n = \frac{M_{n1} \Phi_1}{r_1} + \frac{M_{n2} \Phi_2}{r_2} + \frac{M_{n3} \Phi_3}{r_3} + \cdots + \frac{M_{n8} \Phi_8}{r_8}$$

i_n, r_n, and Φ_n are respectively the current in, the resistance of, and the maximum magnetic flux through, the nth annulus. The M's are the coefficients of self and mutual induction of the annuli.

The values of the coefficients were evaluated and the equations solved, giving the currents in the annuli, for a sine wave current whose maximum value in each coil was 0.085 amp., at a frequency given by $\omega = 10^5$. The current in an annulus may be expressed as follows $i_n = I_n \sin(\omega t + \theta_n)$. In the 4th and 5th columns of Table I. are given the values of I_n and θ_n for the successive annuli, beginning at the center. The second, third,

Table I.

I.	II.	III.	IV.	V.	VI.	VII.
n.	d_n Cm.	$r_n \times 10^3$ Ohms.	I_n Amperes.	θ_n Degrees.	F_n Dynes.	$A_n \times 10^7$ Cm.
1.....	0.97	5.67	1.71	56° 58′	4	0.30
2.....	2.26	12.1	2.33	43° 16′	73	2.36
3.....	3.55	20.7	2.81	41° 58′	345	7.10
4.....	4.84	28.4	3.11	40° 26′	388	5.85
5.....	6.13	35.8	3.32	38° 38′	511	6.08
6.....	7.42	43.3	2.89	43° 19′	768	7.55
7.....	8.71	50.8	2.77	43° 41′	1022	8.56
8.....	10.00	58.3	2.87	42° 52′	1263	9.22

and sixth columns of this table give respectively the diameters and resistances of the annuli, and the maximum values of the electromagnetic force acting on them. The latter are the products of the maximum current in each annulus, its circumference, and the corresponding radial component of the magnetic field for 1 amp. of direct current in each coil. The current in each annulus and the force acting on it are in phase, but the phases of the total instantaneous force and current differ slightly. These latter are given respectively by $f_t = 4423 \sin(\omega t + 41° 30')$, and $i_t = 22 \sin(\omega t + 42° 25')$.

3. *The Amplitude of Vibration of the Diaphragm, and the Amount of Sound Energy it Emits.*—From the above, the forces on the various parts of the diaphragm are nearly in phase; particularly so for those places where the force is large. Consequently, the diaphragm may be considered to vibrate as a whole. It is practically aperiodic for any frequency concerned, so that its elasticity may be neglected. The equation of motion is then

$$m\frac{d^2x}{dt^2} + a\frac{dx}{dt} = F \sin \omega t,$$

where m is the mass of the diaphragm, a is the dissipative factor, and F is the maximum periodic force. The solution of the equation gives for the amplitude of vibration,

$$A = \frac{F}{\omega \sqrt{a^2 + (m\omega^2)}} .$$

The dissipative factor a is made up of two parts; one due to internal friction in the diaphragm, and the other to the emission of sound energy. The former is readily seen to be negligible compared to $m\omega$, while the latter is equal to the product of the velocity of sound, the density of air, and the area of the diaphragm. For $\omega = 10^5$, a^2 is only 0.0025 of $(m\omega)^2$, and consequently it may be neglected. The amplitude then becomes $A = F/m\omega^2$. Substituting $F = 4423$ dynes, $m = 0.60$ gm. and $\omega = 10^5$, the amplitude comes out 7.37×10^{-7} cm. The sound energy emitted from both sides of the diaphragm per second is 9.1 ergs. By increasing both the direct current and the alternating current in the coils five-fold, which is feasible, the amplitude of vibration would be 25, and the energy output 625 times as great; *i.e.*, an output of 5.7×10^3 ergs/sec.

A better idea of the actual performance of the diaphragm is obtained by calculating the amplitudes of the separate annuli. Making the same assumptions as before these amplitudes were found and are given in the seventh column of Table I. An appendix to this paper gives some measurements of the amplitude at various places on the diaphragm.

From the current equations and the preceding discussion it is seen why a thin diaphragm should be used. For high frequencies r_n/ω^2 is small compared to a_{nn}, so that the currents in the diaphragm, and the forces acting on it are independent of its resistance. Increasing the thickness, therefore, does not appreciably increase the force, so that the increased mass results in a proportionally decreased amplitude of vibration. At low frequencies where r_n/ω^2 is of more importance, a thin diaphragm is still preferable, although the advantage is not so marked.

An iron diaphragm will not execute a simple harmonic motion with a sine wave current in the coils, for the magnetic flux through such a diaphragm will not be proportional to this current.

III. Some Applications of the Instrument.

1. *Precision Source of Sound.*—A practically pure tone can be obtained whose frequency and intensity can be maintained practically constant for an indefinite period, can be varied continuously over a very wide range, and can be determined with considerable accuracy. The practical absence of eddy current and magnetic hysteresis energy losses makes it possible to operate the instrument at very high frequencies. The natural period of the diaphragm is so low that it introduces no irregularities in the response in the region of operation.

Mr. C. E. Lane has recently used this instrument to determine the minimum flux of sound energy for audition at several frequencies, and it is intended that this work shall be carried further in the near future. In this connection it may be mentioned that the instrument may be constructed with one coil, so that one side of the diaphragm is free. This has the advantage that the waves are unbroken in leaving the instrument. The resulting tone is somewhat impure, because the radial component of the magnetic field, having an alternating component, is no longer constant. The impurities consist of the octave and higher partials of the fundamental, and can be eliminated by a sound filter. With a direct current large compared to the alternating current, these impurities are negligible. Above 10,000 vib./sec. the impurities are inaudible unless the fundamental is very intense.

The instrument is suitable for the demonstration of diffraction, interference, and reflection effects. At high frequencies, the sound goes out in a well-defined beam, which makes possible some very striking qualitative demonstrations.

For reproducing speech the instrument promises interesting development. It has been used successfully as a generator and as a receiver of voice currents. The coils were specially designed to suit each of these uses. As a generator, the vibration of the diaphragm induces alternating currents in the coils, and these currents are fed into a thermionic amplifier. The voice spoken into one instrument is reproduced with remarkable faithfulness in another connected in the plate circuit of the amplifier. This is due partly to the absence of eddy current and magnetic hysteresis energy losses, and partly to the aperiodicity of the diaphragm. As a loud-speaking generator of sound, the instrument has been used to address an audience of more than one hundred persons. The distinctness of the words, and the quality of the voice of the instrument approached very closely those of the speaker who operated the generator of voice currents.

For voice frequencies the current equations are much simplified. Only the terms containing r_n/ω^2 and the cosine terms need be retained, so that the diaphragm currents are approximately proportional to the frequency, and are nearly in phase. Consequently, the force acting on the diaphragm, for a given alternating current in the coils, is proportional to the frequency, and the amplitude of vibration is inversely proportional to the frequency. This would cause distortion if the voice currents were of the same wave shape as the sound waves which gave rise to them. But if the same kind of instrument is used as a generator, the wave form of its electromotive force is such that the distortion arising in the receiver results in the production of sound waves of the

same character as the original ones. As a matter of fact, actual trials have shown that the distortion, as perceived by the ear, even when using a carbon granule transmitter, is very small.

IV. Appendix. Measurements of the Amplitude of Vibration of the Diaphragm.

Mr. C. E. Lane, while a graduate student in this laboratory, conducted the experimental work described below. Using an electric micrometer for amplitude measurements, the amplitude of vibration at a definite frequency, of an ordinary telephone receiver, was first shown to be proportional to the current through the receiver, and then the ratio of amplitude to current was determined for several frequencies. The tone generator and telephone receiver were excited by alternating current of the same frequency, and a brass tube, of internal diameter 0.4 cm., leading to a tuned resonator carrying a Rayleigh disc, was placed close to the diaphragms, alternately of the tone generator and the telephone receiver. The current in the latter was adjusted till the deflection of the disc was the same for the two. The amplitude for the telephone receiver was calculated from the amplitude-current ratio, and it was assumed that this also gave the amplitude for the tone generator. In this manner the amplitude was determined at various places on the diaphragm, and its distribution was shown to agree closely with that given in Table I. The root mean square of the amplitude was calculated for the whole diaphragm and compared with the amplitude calculated as outlined in section II. Table II. shows the results of these measurements reduced to the standard condition of 1 ampere of direct current and 0.1 ampere of alternating current in the coils. The measured and calculated amplitude agree within the limits of experimental error.

Table II.

Frequency.	Measured Amplitude.	Calculated Amplitude.
1440	4.64×10^{-5} cm.	4.96×10^{-5} cm.
1600	4.16 "	4.52 "
2200	4.04 "	3.24 "
3700	1.72 "	1.88 "

The writer takes pleasure in acknowledging the assistance rendered by Mr. C. E. Lane and other students in this laboratory, in parts of this work. Credit is also due Mr. J. B. Dempster for suggestions in design and help in the construction of apparatus.

State University of Iowa,
Iowa City, Iowa,
October 5, 1921.

OMETER HAVING FLUXMETER CHARACTERISTICS.

By Paul E. Klopsteg.

Synopsis.

Deflection of an ideal fluxmeter in which the coil has great damping control but no torsional control, and has negligible inductance compared with its resistance, is shown to be directly proportional to the current and to the time during which it flows, for the range through which the magnetic torque is proportional to the current.

Measurement of time intervals with such a fluxmeter. In practice it would be necessary to calibrate the instrument, but the relation between deflection and time, for a constant current, should be approximately linear. A great advantage is that the range may be varied at will by proper control of the current.

SEVERAL years ago the writer published[1] the results of an investigation into the possibility of using a moving-coil galvanometer for the measurement of time intervals of the same order of magnitude as the half-period of the undamped galvanometer coil. The results of his experiments showed that such intervals, up to 6 seconds, could be measured with a galvanometer of 6.5 seconds' half-period, and that the probable error of a single observation did not exceed 0.5 per cent. In the work cited, results were obtained for two conditions of damping, viz., slightly damped and critically damped motion of the coil.

In the course of a more recent investigation, there was occasion to analyze the motion of a completely damped coil, *i.e.*, a coil without torsional control, as in the ideal fluxmeter, when the same conditions were imposed as have been outlined in the previous paper. The method of analysis may be briefly summarized as follows:

1. Set up the equation of motion of the coil, assuming zero torsional control.

2. From this equation, determine the angular position, θ_τ, and angular velocity, ω_τ, of the coil, initially at rest, at an instant τ seconds after a steady current has been started flowing in the coil.

3. Assuming that at the instant τ the current is interrupted, substitute the values θ_τ and ω_τ as initial conditions into the equation of motion of the coil, which, beginning at the instant τ, experiences no torque other than damping.

[1] Physical Review, VIII., 195, 1916.

4. Solve the resulting equation for the maximum angle of displacement, θ_m, in terms of τ.

Having obtained an expression involving the variables θ_m and τ—the other quantities being constant and determinable—the expression in the earlier work was made the basis for time measurement by observation of the angle θ_m corresponding to the unknown time interval, τ, during which a steady current passed through the galvanometer. In the present work we arrive at an expression which, on account of its simplicity, is interesting *per se*, and should be even better suited to time measurement than those applying to other conditions of damping, provided a galvanometer with characteristics approaching those of the ideal fluxmeter is used.

In the derivation, the major steps of which are reproduced below, the following symbols are employed, which are the same as those used in the writer's previous papers on galvanometers.[1] τ = time interval to be measured; θ = angular displacement of coil at time t; ω = angular velocity of coil at time t; θ_m = angle of maximum deflection; I_0 = moment of inertia of coil; $2f$ = proportionality constant between damping moment and angular velocity of coil; M = electromagnetic moment of coil; q^2 = elastic torque constant of suspensions; i = steady current impressed on circuit. Other designations are introduced as required. The principal assumptions to be made are that within the angle θ_m the magnetic field shall be uniform and radial, with resulting constant value for M; and that the inductive part of the reactance of the coil circuit shall be very small compared with the pure resistance, so that current growth and decay in this circuit are practically instantaneous.

Step 1.—The equation of motion, since the elastic torque constant $q^2 = 0$, is

$$\ddot{\theta} + \frac{2f}{I_0}\dot{\theta} = \frac{Mi}{I_0}\,. \tag{1}$$

Step 2.—When $t = \tau$, this equation leads directly to

$$\theta_\tau = \frac{Mi}{2f}\left[\tau + \frac{I_0}{2f}\left(\epsilon^{-2f\tau/I_0} - 1\right)\right], \tag{2}$$

and

$$\omega_\tau = \dot{\theta}]_{t=\tau} = \frac{Mi}{2f}[1 - \epsilon^{-2f\tau/I_0}]. \tag{3}$$

Step 3.—At the instant τ, the current is interrupted, and the resultant orque on the coil vanishes. The general equation of motion then becomes

$$\ddot{\theta} + \frac{2f}{I_0}\dot{\theta} = 0, \tag{4}$$

[1] PHYS. REV., V., 266, 1915; VII., 633 and 640, 1916; VIII., 195, 1916; XV., 12, 1920.

which has the general solution

$$\theta = c_2 - \frac{c_1}{2a}\epsilon^{-2at}. \tag{5}$$

where c_1 and c_2 are integration constants, and $a = f/I_0$. To evaluate these, we impose the conditions: $t = 0$, $\theta = \theta_\tau$, $\dot{\theta} = \omega_\tau$, and find

$$\theta = \theta_\tau + \frac{I_0}{2f}\omega_\tau(1 - \epsilon^{-2ft/I_0}). \tag{6}$$

Step 4.—From inspection of equation (6) we see that θ has its greatest value θ_m when t is infinite, and that this value is given by

$$\theta_m = \theta_\tau + \frac{I_0}{2f}\omega_\tau. \tag{7}$$

Into equation (7) we introduce the values of θ_τ and ω_τ given in (2) and (3) and, upon simplifying, find

$$\theta_m = \frac{Mi}{2f}\tau. \tag{8}$$

Equation (8) shows that under the assumed conditions of an ideal fluxmeter, when used as an instrument for time measurement, the angle of deflection is accurately proportional to the time interval during which the current i is sent through the coil.

Under practical conditions, since the elastic torque of a fluxmeter suspension is never quite zero, such an instrument should be calibrated. This can readily be done by some such method as has been previously described.[1] The time scale will not depart far from uniformity, and its range can be varied at will by proper control of the current.

Central Scientific Company,
Chicago, Ill.,
August 15, 1921.

[1] Loc. cit., p. 204.

THE EFFECT OF DAMPING ON THE WIDTH OF X-RAY SPECTRUM LINES.

By G. E. M. Jauncey.

Synopsis.

Width of X-ray Spectrum Lines Due to Damping.—(1) Assuming exponential damping, the equation for the ether vibrations, $y = e^{-kt} \sin (pt + A)$, is developed as a Fourier integral and thus a *theoretical relation of the width to the damping factor* is found. If we define the width of the line as the range in wave-length throughout which the intensity is greater than half the maximum intensity of the line, then $x\lambda/\lambda = dp/p = 2k/p$, very closely.

(2) *Theoretical Variation with Wave-length.* Assuming in addition that k has the value given by the classical theory of a single radiating electron, $d\lambda = 2k\lambda/p = 4\pi e^2/3mc^2 = 1.2 \times 10^{-4}A$, *i.e.*, $d\lambda$ is independent of wave-length.

(3) *Comparison with Observation.*—A. H. Compton has found the widths of the W lines, $\lambda\lambda$ 1.242 and 1.279A, to be about $9 \times 10^{-4}A$, nearly eight times the above value. The discrepancy indicates that either the theory is incorrect, or the measurement is wrong, or that damping is not the chief cause of the observed width.

In this issue of the Physical Review, Professor A. H. Compton describes experiments in which he has measured the width of x-ray spectrum lines. The lines used were the tungsten lines $\lambda = 1.242$ and $\lambda = 1.279$ Å.U. After correcting for the angular aperture of the slits, the angular faults of the crystal grating, and the finite resolving power of the grating, Professor Compton finds that the width due to the non-homogeneity of the x-rays is given by $(\delta\lambda/\lambda) > 0.0007 \pm .00014$, or a width of the order of, but greater than, 0.5 minute of arc in the first order spectrum as reflected from calcite. It is the purpose of this paper to examine into a possible explanation of this width on the assumption that the wave motion sent out by the oscillator emitting x-rays can be represented by an equation of the type $y = e^{-kt} \sin [p(t - x/c) + A]$. This damped harmonic motion can be represented by a Fourier's integral. We shall assume that the oscillations begin at time $t = 0$, so that $y = F(t) = 0$ for $0 > t > -\infty$, but that $y = F(t) = e^{-kt} \sin (pt + A)$ for $\infty \geqq t \geqq 0$.

The formula for the expression of $F(t)$ as a Fourier's integral is well known[1] and we obtain

[1] Cf. Byerly, Fourier Series and Spherical Harmonics, p. 54.

$$e^{-kt}\sin(pt+A) = \frac{1}{\pi}\int_0^\infty \frac{d\omega\cdot\sqrt{C^2+D^2}\cdot\cos(\omega t-\tan^{-1}D/C)}{(p^2-\omega^2+k^2)^2+4k^2\omega^2},$$

where

$$C = p(p^2-\omega^2+k^2)\cos A + k(p^2+\omega^2+k^2)\sin A,$$

and

$$D = 2kp\omega\cos A - \omega(p^2-\omega^2-k^2)\sin A.$$

If now I_ω represents the intensity of the radiation of frequencies between

$$\frac{\omega-(\delta\omega/2)}{2\pi} \text{ and } \frac{\omega+(\delta\omega/2)}{2\pi},$$

we have

$$(1)\quad \frac{I_\omega}{I_p} = \frac{\omega^2}{p^2}\times\frac{(p\cos A+k\sin A)^2+\omega^2\sin^2 A}{p^2+2kp\cos A\sin A+k^2\sin^2 A}\times\frac{k^2(4p^2+k^2)}{(p^2-\omega^2+k^2)^2+4k^2\omega^2},$$

where I_p is the intensity when $\omega = p$. In Professor Compton's experiments the intensities were plotted against the wave-lengths and the difference between the two values of λ for which the intensity was one half of that of the center of the line was taken as $\delta\lambda$. We shall therefore take $I_\omega/I_p = \frac{1}{2}$, and

$$\frac{\omega-p}{p} = \frac{1}{2}\frac{\delta\lambda}{\lambda} = .00035 = a.$$

Since ω is very nearly equal to p and since therefore $p^2\cos^2 A + \omega^2\sin^2 A$ is very nearly equal to p^2, equation (1) reduces to the approximate form

$$(2)\quad \frac{I_\omega}{I_p} = b = \frac{k^2(4p^2+k^2)}{(p^2-\omega^2+k^2)^2+4k^2\omega^2},$$

which is independent of the phase angle A. Solving this equation for k and putting $\omega = p(1+a)$ where a is small, we obtain approximately

$$(3)\quad k = \frac{2\pi ac}{\lambda}\sqrt{\frac{b}{1-b}},$$

where $p = 2\pi c/\lambda$ and c is the velocity of light in vacuo. If b is taken as $\frac{1}{2}$, $k = pa = \omega - p$.

In Professor Compton's experiments $a = .00035$, $b = \frac{1}{2}$, and $\lambda = 1.242$ Å.U. for one of the lines observed. These values give $k = 5.3\times 10^{15}$ sec^{-1}. The amplitude of the vibration $y = e^{-kt}\sin(pt+A)$ is therefore damped to $1/e$ of its initial value in 1.89×10^{-16} secs. In this time the oscillator makes 457 vibrations and the energy of the wave train given

out by the oscillator therefore becomes damped to $1/e$ of its value in 229 wave-lengths.

Professor Compton gives the damping factor due to radiation for a single electron on the classical electrical theory as being equal to

$$\frac{4\pi^2}{3} \cdot \frac{e^2}{m\lambda^2 c} \cdot \tag{4}$$

For $\lambda = 1.242$ A.U. this gives $k = 7.2 \times 10^{14}$ sec^{-1}, the amplitude being damped to $1/e$ of its value in 3,360 vibrations. Assuming that the damping factor of the emitted x-rays is equal to that of the oscillator, we have from (3) that a, or $\delta\lambda/2\lambda$, is equal to

$$\frac{k\lambda}{2\pi c}\sqrt{\frac{1-b}{b}} = .000047. \tag{5}$$

This corresponds to a width of 4 seconds of arc in the first order spectrum as reflected from calcite, the experimental value being greater than 30 seconds of arc.

The inconsistency between the damping factor as calculated by means of Fourier's integral from the observed width and that as calculated from formula (4) may be due to, (*a*) the incorrectness of the formula (4) as applied to the x-rays emitted by the oscillator, (*b*) the inaccuracies of the experiments measuring the width, (*c*) the possibility that the spectrum lines are made up of a finite number of lines close together, and (*d*) the possibility that the oscillation at a point in the ether due to the emitted x-rays cannot be represented by an equation of the form $y = e^{-kt} \sin (pt + A)$. It is hoped in the near future to make a redetermination of the width experimentally so as to eliminate (*b*).

The damping of the oscillator which emits any electromagnetic radiation must tend to broaden the spectrum line observed. This is true for light waves as well as for x-rays. From formula (4) it is seen that for light waves

$$a = \frac{\delta\lambda}{2\lambda} = 1 \times 10^{-8}$$

approximately. The broadening of the spectrum lines for ordinary light due to damping is therefore too small to be observed. In the x-ray case, however, an appreciable part of the width (about 13 per cent. according to Professor Compton's experiments) is due to damping. It is interesting to note that from the formulas (4) and (5) $a = \delta\lambda/2\lambda$ varies as $1/\lambda$, so that $\delta\lambda$ is constant for all values of λ throughout the x-ray

and light spectra.[1] This value of $\delta\lambda$ due to damping equals 1.2×10^{-4} Å.U. approximately.

The writer's thanks are due to Professor Compton of Washington University for his interest in the preparation of this paper.

Physics Laboratory,
Washington University,
St. Louis,
June 8, 1921.

[1] The writer is informed that Mr. C. G. Darwin, of Cambridge University, England, has also noted this interesting fact.

THE WIDTH OF X-RAY SPECTRUM LINES.

By Arthur H. Compton.

Synopsis.

Width of X-ray Spectrum Lines.—(1) *Four causes* are discussed: (*a*) the width of the slit employed, (*b*) angular imperfections of the crystal, (*c*) finite resolving power of the crystal grating, and (*d*) lack of homogeneity of the x-rays. The effect of the first two causes is independent of the angle of reflection and therefore the same for all orders and all lines; the effect of the third is shown to vary as $1/\sin\theta\cos\theta$ and therefore to decrease as θ increases up to 45°; while the effect of the last is equal to $(d\lambda/\lambda)\tan\theta$ and therefore increases with θ. (2) *Measurements of two tungsten lines*, λ 1.242 and 1.279 Å, in the first four orders from the cleavage faces of calcite and rock-salt, are given. The fact that in both cases the width is least for the second order and greatest for the fourth order shows that both the third and fourth causes contribute measurably to the observed width, as well as the first two.

Lack of homogeneity of tungsten x-ray lines computed from the above measurements comes out greater than $0.0007\lambda \pm .00013\lambda$, which is about 0.5′ for the first order. This cannot be explained as a Doppler effect or as due to the damping of the electronic motion; however it is in accord with the complexity of the lines as predicted by Sommerfeld's theory of elliptic electronic orbits.

SEVERAL years ago the writer performed a series of experiments designed primarily to measure the relative intensities of the different orders of x-ray spectrum lines reflected from crystals of rock-salt and calcite. A recording x-ray spectrometer, which has previously been described,[1] was employed, the intensities of the lines being taken proportional to the area under the curves on the record representing the different spectrum lines. These intensity measurements, in which cleavage faces of the crystals were employed, were later found to be valueless as a test of the theory of reflection, because of the selective absorption which occurs at the angle of maximum reflection from a cleavage face.[2] The results show, however, an interesting broadening of the lines in the higher orders.

The width of the spectrum lines was measured at a point midway between the peak of the curve and a base-line representing the intensity of the general radiation. The average values thus found for the tungsten lines $\lambda = 1.242$ and $\lambda = 1.279$ Å.U. are as follows:

[1] A. H. Compton, Phys. Rev., 7, 658 (1916).

[2] A. H. Compton, Phys. Rev., 10, 95 (1917); W. L. Bragg, James and Bonsanquet, Phil. Mag., 41, 309 (1921).

TABLE I.

Width in Minutes of Arc at Mid-point of Line.

Crystal.	First Order.	Second Order.	Third Order.	Fourth Order.
Calcite	16.3 ± .6	16.0 ± .36	17.3 ± .7	18.3 ± .12
(Calc.)	15.4	(16.0)	16.7	(18.3)
Rock-salt	20.1 ± .5	18.9 ± .3	20.3 ± .6	21.2 ± 1.2
(Calc.)	18.3	(18.9)	19.8	21.5

The size of the slits remained unchanged throughout the experiments. The measurements on the second and fourth orders of reflection from calcite are the most valuable, because these two lines are of nearly equal intensity, which tends to eliminate any consistent errors.

The observed width of a spectrum line may result from four different causes, (*a*) the angular aperture of the slits, (*b*) angular faults in the crystal grating, (*c*) the finite resolving power of the grating, and (*d*) the lack of homogeneity of the incident x-rays.[1] The width due to the size of the slits will obviously be the same at all angles. That due to angular faults in the crystal may vary somewhat according to the part of the crystal which is exposed to the x-rays, but should on the average be the same for all angles of reflection. It is clear that no crystal will act as a perfect grating, and that the resolving power will depend upon the size of the portions of the crystal which are effectively perfect. It can be shown[2] that if these perfect portions are assumed to be parallelopipeds of width along the crystal face δx, height δy and depth into the crystal δz, the effective width of the line (area/height) in radians is:

$$(1) \qquad \delta\theta_c = \frac{\lambda}{2\delta x \sin\theta} \quad \text{for} \quad \frac{\delta x}{\delta z}\tan\theta < 1,$$

$$\delta\theta_c = \frac{\lambda}{2\delta z \cos\theta} \quad \text{for} \quad \frac{\delta x}{\delta z}\tan\theta > 1,$$

where λ is the wave-length and θ the glancing angle. In crystals of rock-salt and calcite δx and δz are doubtless on the average about equal, so that $\delta\theta_c$ will be a minimum for $\theta = \pi/4$, increasing symmetrically for smaller and larger angles. Because of chance variations in δx and δz

[1] In the experiments here described, the beam incident upon the crystal was collimated by a pair of narrow slits, and the opening at the ionization chamber was wide enough to admit all the reflected rays. With Bragg's method of using narrow slits near the x-ray tube and at the ionization chamber and a wide slit at the crystal, the width also depends upon a fifth factor, the penetration of the x-rays into the crystal.

[2] This follows (after considerable reduction) from the results given by the writer in THE PHYSICAL REVIEW, 9, 37 (1917).

for the different component crystals, the change from $\delta\theta_c \propto 1/\sin\theta$ to $\delta\theta_c \propto 1/\cos\theta$ will be gradual. Thus it appears that the width of the line due to this finite resolving power should vary approximately according to the expression

$$\delta\theta_c \propto 1/\sin\theta\cos\theta. \tag{1a}$$

The angular width due to a given range of wave-lengths $\delta\lambda$ in the incident x-rays may be found by differentiating $\lambda = 2D\sin\theta/n$ with respect to θ. Thus we find that

$$\delta\theta_d = \frac{n\delta\lambda}{2D\cos\theta} = \frac{\delta\lambda}{\lambda}\tan\theta. \tag{2}$$

The total width of the line is a rather complicated function of $\delta\theta_a$ due to the width of the slits, $\delta\theta_b$ due to angular imperfections of the crystals, and $\delta\theta_c$ and $\delta\theta_d$ given by equations (1) and (2) respectively. Thus we may write

$$\delta\theta = F(\delta\theta_a, \delta\theta_b, \delta\theta_c, \delta\theta_d).$$

The function F will increase with every increase in any variable $\delta\theta_r$, in such a manner that $\delta\theta$ will be greater than any one of its components but will be less than the sum of all four. The form of this function cannot be determined unless we know the exact manner in which the intensity varies with the angular distance from the center of the line on account of each factor contributing to the width. Lacking such definite knowledge, a simple graphical analysis shows that an increase in $\delta\theta_r$ will result in an increase in $\delta\theta$ of the same order of magnitude but smaller than the change in $\delta\theta_r$, *i.e.*,

$$1 > \frac{\partial\delta\theta}{\partial\delta\theta_r} > 0.$$

Furthermore by Taylor's theorem, to a first approximation,

$$\delta\theta = \delta\theta_0 + \frac{\partial\delta\theta}{\partial\delta\theta_a}\Delta\delta\theta_a + \frac{\partial\delta\theta}{\partial\delta\theta_b}\Delta\delta\theta_b + \frac{\partial\delta\theta}{\partial\delta\theta_c}\Delta\delta\theta_c + \frac{\partial\delta\theta}{\partial\delta\theta_d}\Delta\delta\theta_d, \tag{3}$$

where $\Delta\delta\theta_r$ represents a change in $\delta\theta_r$.

In the experiments using a calcite crystal, $\delta\theta_a$ and $\delta\theta_b$ remain constant, $\delta\theta_c$ decreases with θ (up to 45°), and $\delta\theta_d$ increases with θ. The observed increase in the width of the lines in the higher orders therefore means that $(\partial\delta\theta/\partial\delta\theta_d)\Delta\delta\theta_d$ is more prominent than $(\partial\delta\theta/\partial\delta\theta_c)\Delta\delta\theta_c$. If we neglect the term in $\delta\theta_c$ and compare the value of $\delta\theta$ at two angles θ_1 and θ_2, it follows from expression (3) that

$$\delta\theta_2 - \delta\theta_1 = \frac{\partial\delta\theta}{\partial\delta\theta_d}(\delta\theta_{d_2} - \delta\theta_{d_1})$$

whence according to equation (2)

$$\frac{\delta\lambda}{\lambda} = \frac{\partial\delta\theta_d}{\partial\delta\theta}\,\frac{\delta\theta_2 - \delta\theta_1}{\tan\theta_2 - \tan\theta_1}\,. \tag{4}$$

Substituting the values of $\delta\theta$ observed in the second and fourth orders from calcite, noting that the angles θ_2 and θ_4 are 24.2° and 55.2° respectively and that $\partial\delta\theta_d/\partial\delta\theta$ is of the order of but greater than unity, we find that $\delta\lambda/\lambda$ is of the order of but greater than $0.0007 \pm .00014$. The values calculated in the second row of Table I. result from the further approximation that $\partial\delta\theta_d/\partial\delta\theta$ is constant for all values of $\delta\theta_d$. If we take this constant as unity, we find 0.0007 for the minimum value of $\delta\lambda/\lambda$, and 0.5′ for the minimum value of the width of the first order spectrum line due solely to lack of homogeneity of the x-rays. The observations on rock salt lead to values of the same order of magnitude.

The widths calculated for the lines reflected from calcite agree well with the experiments except in the first order. This line appears to be too broad, as we have noticed should result from the small resolving power if the crystal is sufficiently imperfect. The imperfection of the rock-salt crystal as compared with calcite shows itself both in the greater value of the constant $\delta\theta_b$ for rock salt, indicated by a greater width in all orders, and by the greater difference between the breadth of the first and second orders. According to equation (1*a*) the broadening due to this imperfection is nearly proportional to $1/\sin\theta\cos\theta$, *i.e.*, to 2.5, 1.3, 1.0 and 1.1 in orders 1, 2, 3 and 4 respectively. A difference in breadth of 1.8′ between the first and second orders of rock salt [1] will therefore correspond to a difference of only 0.3′ between the second and fourth orders. The unmistakable broadening of the higher orders can apparently be accounted for only by a true lack of homogeneity of the x-ray spectrum line. Thus it appears that all the terms of expression (3) have values that are appreciable in experiment.

It is of interest to consider the possible origin of the observed non-homogeneity of the x-rays. Let us consider first the width to be expected on the basis of the Doppler effect. The average velocity of the tungsten molecules in the target at 2000° K. is only about 10^{-6} times the velocity of light, and could therefore account for only a negligible part of the non-homogeneity of the x-rays. The velocity of the thermal motion of an electron, according to the principle of equipartition of energy, would give rise to a Doppler effect of the required order of magnitude; but the fact that the spectrum lines are characteristic of the tungsten

[1] This difference corresponds to a value of $\delta\theta_c > 3.2'$ in the first order. Thus by equation (1), $\delta x < c.\ 2700\lambda = 4.5 \times 10^{-5}$ cm.

atom indicates that it is not a free electron which emits the radiation, but one which is a part of the atom.

The damping of the electron's linear oscillations due to its own radiation, on the other hand, results in a width which is not negligible. The damping factor for a single oscillating electron is

$$\frac{4\pi^2}{3}\frac{e^2}{m\lambda^2 c},$$

where e, m and C have their usual significance. For $\lambda = 1.25$ Å.U., this means that the wave will be damped to $1/e$ of its amplitude in 3,400 vibrations. By an application of Fourier's integral, Professor Jauncey finds[1] that the effective width of the line due to this damping is about 0.06 minute of arc in the first order, which is 12 per cent. of the minimum width found experimentally.

It appears probable that the chief cause of the non-homogeneity observed in these experiments is that the lines themselves are complex. Thus the line $\lambda = 1.279$ is known to have a faint companion 0.008 Å.U. distant which was not separated in the first and second orders by the slits employed; and according to Sommerfeld's theory of the fine structure of spectrum lines, the line 1.242, on which most of the fourth order measurements were made, should have faint satellites at distances of about 0.0007, 0.002 and 0.006 Å.U.

The experiments described in this paper were performed at Palmer Physical Laboratory, Princeton University.

WASHINGTON UNIVERSITY,
SAINT LOUIS,
July 18, 1921.

[1] Cf. G. E. M. Jauncey elsewhere in this number of the PHYSICAL REVIEW.

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THE

PHYSICAL REVIEW.

ON THE GAMMA-RAY ACTION OF EXTENSIVE FLAT RADIUM PREPARATIONS AT DIFFERENT DISTANCES WITH AND WITHOUT ABSORBING MATERIALS.

By Victor F. Hess.

Synopsis.

Intensity of gamma-radiation from a radium-covered disk at points along the central normal, with and without absorbing layers, is of interest in connection with the use of radium applicators for gamma-ray treatments. By integrating the effects of narrow rings of the active material, a *theoretical formula is derived* for the intensity at a distance p from a disk of radius R if the rays go through one or more filters whose absorptions are known and through a thickness of tissue h_0. This formula involves the so-called exponential integral for which tables are available. Numerical values have been calculated for certain special cases and these are given in two tables which enable the intensity to be determined at various distances from any uncovered disk in air and also from any disk covered by a layer of brass 2 mm. thick. A given amount of radium spread on a 4 cm. disk gives at distances greater than 4 cm. about the same intensity as when concentrated on the end of a small tube, but the effect near the active layer is over ten times less intense in the former case. This result shows that burns of the skin may be avoided by using sufficiently large disks without decreasing the depth action materially.

New unit of gamma-ray intensity is proposed, to be called a *milli-eve* and to be defined as the intensity at a distance of 1 cm. from a point-shaped radium preparation of one milligram.

Introduction.

THE "flat radium applicators" consist mostly of a metallic disk covered on one side with a lacquer, with which some radium salt is mixed. The shape of the disk may be rectangular or circular. The calculation is given for circular disks and may be applied for other shapes with sufficient accuracy. In order to cut off all alpha and most of the beta rays the surface of the radium disk is covered by a metallic disk. This "filter-disk" consists of brass, copper or similar materials and has a thickness of 1–2 mm. A second filter, made of a material of low atomic weight (celluloid, rubber, etc.) is applied to absorb the secondary β-rays, which come out from the metal disk. The thickness of

this second disk is relatively small (1–3 mm.). The absorption of the primary γ-rays in this layer may therefore be neglected.

THEORY OF THE GENERAL CASE.

Fig. 1 illustrates the general case. The radioactive layer (circular area of radius R) is considered as a disk of infinitely small thickness and σ represents the quantity of radium per sq. cm. The metallic filter has a thickness d_0 and is applied directly below the radioactive disk.

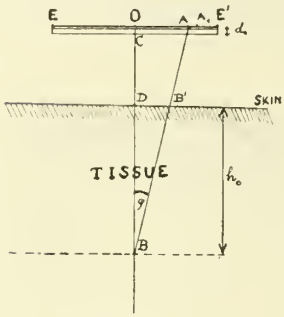


Fig. 1.

The radius of the disk is

$$R = OE, \qquad R = OE'.$$

The point at which the intensity of the γ-rays is considered is B.

We call the distances

$$OA = r, \qquad OB = p,$$
$$OC = d_0, \qquad BD = h_0.$$

The last-mentioned letter indicates the thickness of tissue, which has to be traversed before point B is reached.

Now we take an arbitrary point A on the radioactive disk and consider the action of the ring-shaped element of area of the width $AA_1 = dr$ at the point B.

The action of the γ-rays of this element at B without any absorption would be

$$dQ = K \cdot \frac{2\pi r \cdot dr \cdot \sigma}{p^2 + r^2},$$

where K indicates the so-called "Eves number"; that is the number of pairs of ions, generated by the γ-rays of 1 g. of radium at the distance 1 cm. from the source of rays.

The γ-rays coming from A traverse the metallic filter and the tissue in an oblique direction according to an angle $\varphi = \sphericalangle OAB$. We call the absorption coefficient in the metal-filter μ, in the tissue ν.

The factors which express the real absorption of γ-rays in the filter and the tissue become therefore

$$e^{-\frac{\mu d_0}{p}\sqrt{p^2+r^2}} \quad \text{and} \quad e^{-\frac{\nu h_0}{p}\sqrt{p^2+r^2}}.$$

Their product corresponds to the total absorption.

Thus we get for the real intensity of γ-rays at point B, created by the

rays of the ring-shaped element dr, the expression

$$dQ = 2\pi K\sigma \frac{rdr}{p^2 + r^2} \cdot e^{-\frac{\mu d_0 + \nu h_0}{p}\sqrt{p^2+r^2}}.$$

For simplicity we may write

$$\frac{\mu d_o + rh_o}{p} = b.$$

This expression represents a constant for every special distance.

To find the total amount of the γ-ray intensity at B we have to integrate dQ over the whole area of the disk. Thus we obtain the integral

$$Q = 2\pi K\sigma \int_o^R \frac{re^{-b\sqrt{p^2+r^2}}}{p^2 + r^2} dr. \tag{1}$$

It is easy to reduce this integral to a known form by introducing the new variable $u = b \cdot \sqrt{p^2 + r^2}$.

Therefore the integral becomes

$$Q = 2\pi\sigma K \int_{b.p}^{b.\sqrt{p^2+r^2}} \frac{e^{-u}}{u} du \tag{2}$$

The integral $\int (e^{-u}/u)du$ is commonly called "the exponential integral." Numerical values of this integral are given by J. W. L. Glaisher,[1] W. L. Miller and T. R. Rosebrugh [2] and others.

We call as usual

$$-\int_a^\infty \frac{e^{-u}}{u} du = Ei(-a).$$

The corresponding value of this integral may be taken directly from the tables for all values of a. A transformation of formula (2) leads to the expression

$$Q = -2\pi\sigma K[Ei(-b \cdot p) - Ei(-b \cdot p \sqrt{p^2 + R^2})].$$

After substituting for b we obtain the general solution

$$Q = 2\pi\sigma K\left[Ei\left(-\frac{\mu d_0 + \nu h_0}{p}\sqrt{p^2 + R^2}\right) - Ei(-\mu d_0 - \nu h_0)\right]. \tag{3}$$

By introduction of the numerical values we obtain thus directly the ionization created by the γ-rays at the chosen distance from the disk after allowing for the absorption in the filter and the tissue. When the values of Q for different distances p are calculated the law of decrease of intensity of the gamma-radiation in each special case may be obtained.

[1] J. W. Glaisher, Phil. Trans., Vol. 160, p. 367 (1870).

[2] W. L. Miller and T. R. Rosebrugh, Trans. Roy. Soc. of Canada, 3 Series, Vol. 9, sect. 3, p. 73 (1903).

Formula (3) may be easily applied also in cases, where several different filters are used. In these cases we have simply instead of μd_0 to introduce the sum $(\mu d_0 + \mu' d_0' + \cdots)$ where μ and d_0 denote the absorption coefficients and respective thicknesses of the different filters used.

It can also be seen from formula (3) that Q is independent of the unit of length used for p and R; that it depends only on the ratio $\frac{p}{\sqrt{p^2 + r^2}}$, which is the cosine of the angle subtended by the radius of the disk. Therefore the effect at 4 cm. from a disk of 2 cm. diameter is the same as at a distance of 2 cm. from a disk of 1 cm. diameter. This holds of course only when σ, the quantity of radium per unit of area, is kept constant. In the numerical tables which are given later not σ but the total radium content of disks of different diameters is taken as constant. This corresponds more to the actual conditions of medical use.

Different absorbent materials have the same effect, when the products of absorption coefficient and thickness of layer have the same numerical value. Thus a layer of brass (thickness d_0) and a layer of tissue (h_0) are equivalent, when $\mu \cdot d_0 = \nu \cdot h_0$.

Special Cases.

1. Action of the γ-rays of a radium disk, covered by a metal screen (thickness d_0) in air.

This case is of interest, for it gives the actual amounts of ionization. by the γ-rays of the disk, when no tissue is between the source and the chosen point (for instance a point directly on the surface of the skin). This case corresponds to $h_0 = 0$ and formula (3) changes into the simpler form

$$Q = 2\pi\sigma K \left[Ei\left(-\frac{\mu d_0}{p} \sqrt{p^2 + r^2} \right) - Ei(-\mu d_0) \right] \cdot \qquad (3')$$

2. Action of the radium disk without any absorbing filters: This case is physically not without interest: from this it is possible to judge upon the difference in the distance-action of a disk and an approximately point-shaped source of radiation. For $d_0 = h_0 = 0$ formula (3) becomes indefinite. Thus we have to go back to formula (1). Here the exponential factor becomes 1 and the integral leads to the simple solution

$$Q = 2\pi\sigma K \left[1 \cdot 1513 \cdot \log_{10} \cdot \frac{p^2 + R^2}{p^2} \right] \qquad (1')$$

(for greater convenience in practical cases Briggs's logarithms are introduced).

Practical Applications and Proposal of a New Unit for the Intensities of Action of the γ-Rays.

In the numerical computations of the formulas (1)–(3) given above it will be found troublesome to express Q in terms of K (number of pairs of ions, created per c.c. and sec.), because K is a very high number (*Eve* found, that in air $K = 3 \cdot 9.10^9$ ions/ccm. sec.). In most cases relative numbers, for instance the expressions within the brackets, would suffice.

However, for a greater convenience of use, expecially for physicians, a new unit for γ-ray intensities may be proposed: The action (ionization) of the γ-rays of RaC in equilibrium with 1 gram of radium, given as a nearly point shaped source (very small tube) at the distance of 1 cm. from this source may be called "*1 Eve*." The one thousandth part of this intensity be called "*1 Milli-Eve*." According to this definition[1] a small radium-tube of 50 mg. radium element would give (by its γ-radiation) in the distance 1 cm. 50 Milli-Eves; in 2 cm. (corresponding to the inverse square of distance-law, 12.5 Milli-Eves; in 3 cm. 5.56 Milli-Eves; in 0.5 cm. 200 Milli-Eves, etc.

According to that the total amount of γ-radiation used in one exposure may be expressed in Milli-Eve hours, that is the product of the number of Milli-Eves into the number of hours of exposure.

To express the results of the formulas of this paper in Milli-Eves, we have to consider that according to the definition of this new unit the intensity of a point-shaped and unfiltered radium preparation at 1 cm. distance has to be taken as 100 when a source of 100 mg. is used. When we use a filtration of 2 mm. brass, the intensity at the same distance would be about 90 and all other intensities have to be changed in the same proportion.

In the following tables it is assumed that 100 mg. preparations are used. For other amounts the figures have to be altered accordingly.

The values of the exponential integral $Ei(-a)$ are taken from abbreviated tables, given in Meyer and Schweidler's "Radioactivity" (Teubner, Leipzig, 1916). The coefficient of absorption of the complex γ-radiation of RaB and RaC has been assumed as $\nu = 0.094$ cm. This is an average of experimental values found by G. Failla (Amer. Journ. of Roentgen., Vol. 3, 215–232, 1920) and A. Fernau (Strahlentherapie, Vol. 9, p. 236–254, 1918).

Table I. shows the γ-ray-intensities at different distances from a circular disk (4 cm. diameter), covered uniformly with 100 mg. radium for three cases: without any filter (formula 1′), with a filter of 2 mm.

[1] Prof. A. S. Eve (Montreal, Canada) was the first who determined the absolute values of the ionization of γ-rays at different distances from a known radium source. A. S. Eve. Phil. Mag. (6), 12, 189 (1906); 22, 551 (1911); 27, 39 (1917).

brass (formula 3′) in air and in tissue. Column 3 gives the figures in the case, when the same filtered disk is directly applied above the skin. All figures in this column are considerably lower than in column 2 according to the absorption in the tissue.

TABLE I.

Radium Disk, 4 cm. diameter, 100 mg. Radium.

Distance from the Surface of the Radium Disk (Cm.).	γ-ray Intensities in Milli-Eves.		
	No. 1, Uncovered Disk in Air.	No. 2, Disk Filtered by 2 Mm. Brass in Air.	No. 3, Disk Filtered by 2 Mm. Brass in Tissue.
p = 0.3	107.4	81.2	79.7
0.5	80.0	64.9	61.5
1.0	45.4	38.9	35.4
2.0	19.5	18.1	14.9
3.0	10.3	8.5	6.8
4.0	6.3	5.1	4.2
5.0	4.2	3.4	2.7
6.0	3.0	2.3	1.6
7.0	2.1	1.8	1.1
8.0	1.7	1.4	0.8
10.0	1.1	0.8	0.5

As a second example the intensities of the γ-radiation have been calculated for circular disks of the same radium amount but different diameters, varying from 0.4 to 8.0 cm. The smallest type of these disks corresponds to a practically point-shaped radium-source (very small tube). The figures in the following Table II. are again given in Milli-Eves.

TABLE II.

Distance from the Surface of the Radium Disk in Cm.	γ-ray Intensities (in Milli-Eves) (all Disks Filtered by 2 Mm. Brass).				
	Disk of 0.4 Cm. Diameter.	Disk of 1.0 Cm. Diameter.	Disk of 2.0 Cm. Diameter.	Disk of 4.0 Cm. Diameter.	Disk of 8.0 Cm. Diameter.
p = 0.3	888	528	215	81	24
0.5	341	289	154	65	21
1.0	90	82	72	39	16
2.0	22	22	21	18	9.7
3.0	10	10	9.5	8.5	6.4
4.0	5.6	5.7	5.5	5.1	4.5
5.0	3.6	3.6	3.6	3.4	3.1
6.0	2.5	2.4	2.4	2.3	2.2
7.0	1.8	1.9	1.8	1.8	1.7
8.0	1.4	1.4	1.4	1.4	1.3
10.0	0.8	0.8	0.8	0.8	0.8

It is easily to be seen from this table that the intensities of the γ-rays of the smallest and the largest disk on the surface vary in the proportion 888 : 24; the action in the depth (from 3 cm. on) is nearly the same with all the disks. The use of large radium disks is therefore recommendable in all cases, where the action of points near the preparation itself should be as small as possible (for instance to avoid burns of the skin).

Physical Research Laboratory,
The United States Radium Corporation,
Orange, N. J.,
October, 1921.

PHYSICAL CHARACTERISTICS OF NORMAL AND ABNORMAL EARS.

By John P. Minton.

Synopsis.

Sensitivity Curves for Normal and Abnormal Ears.—Previous investigators have worked only with normal ears and their results are not as a rule corrected for the resonance properties of the diaphragms used. Lord Rayleigh's curves are more reliable but do not extend above 768 double vibrations. In the present work a telephone receiver was used with a natural frequency above the range of the tests, 5,200 d.v., and its vibrational and electrical characteristics were determined so that the vibrational energy of the diaphragm could be calculated for any current of any frequency used. The currents were generated with an audion oscillating circuit, and a Wheatstone bridge was used in measuring the minimum audible current for both normal and abnormal ears; the readings in the case of normal ears were then converted into *minimum vibrational energy* and plotted *as a function of the frequency up to 4,000 d.v.* Curves are given (1) for normal ears; (2) for ears diseased only in the middle ear; (3) for ears diseased only in the internal ear; (4) for ears having a combination of middle and internal ear trouble. The normal ear curve shows a number of characteristic maxima with subsidiary inflections. In *middle ear deafness* the hearing is most deficient for low tones and more nearly normal for high ones, while *inner ear deafness* begins for high pitches and may not affect the hearing for low pitches. Sets of curves show the development of the diseases with time. In true *nerve deafness* cases have been studied in which total deafness appears to exist for a part of the sound spectrum; in one case on record, for instance, 200 billion times the energy required to stimulate the normal ear failed to produce the sensation of sound. Some *conclusions regarding the mechanism of audition* are drawn. The normal ear acts like a complex mechanical or electrical vibrating system whose response depends on many factors including the tympanum, bones, muscles, ear cavities and the internal ear. No resonant frequency can be assigned to any one member of it. When the middle ear mechanism is absent, the internal ear has resonant frequencies different from those of normal ears. The receiving mechanism in the internal ear is arranged in a linear manner beginning with the basal part which probably responds to the high pitched sounds, and each section is sensitive to only a narrow range of frequencies. The probable fact that the high frequency fibers are under greater tension than the lower frequency ones may account for the characteristics of internal ear deafness.

Discussion of Theories of Audition.—The difficulties confronting each theory are briefly pointed out. In some ways the above results tend to confirm the Helmholtz theory, but it is hard to see how any mechanical theory can explain the absolute insensitiveness to a limited range of pitch which has been observed in cases of nerve deafness.

I. Introduction.

THE present work was undertaken in coöperation with Dr. J. Gordon Wilson, Head of the Department of Otology at Northwestern University Medical School. Through this coöperative study much light

has been thrown on the subject of deafness and on the manner in which the normal ear functions. In the present paper are given some of the physical data on normal and abnormal ears, together with a discussion of the theoretical bearing of these data from the viewpoint of the theories of audition.

Inasmuch as the present method of testing involves the use of telephone receivers, it will be well to refer briefly to the work of other investigators who have published results on normal and abnormal ears. Rayleigh has summarized[1] somewhat briefly the early results on the minimum audible current in telephone receivers obtained by Preece, Tait, De la Rue, Brough and Ferraris. Rayleigh found difficulty in harmonizing the results obtained by these investigators with those secured by himself.[2] However, this lack of agreement is not to be wondered at in view of our present knowledge of telephone receivers and particularly in view of the diverse conditions under which the experiments were made.

The early work in this field did not extend above 768 d.v. (double vibrations), so that the sensitivity of the ear could not be estimated over the whole region of frequencies which are necessary for both speech and musical sounds. Rayleigh in his early experiments found a maximum of sensitiveness to receiver-currents in the region of 640 d.v., but he recognized that his data were insufficient to warrant the drawing of this conclusion. It is of interest to note that Rayleigh's maximum corresponds to the position of the first maximum of sensitiveness of some of the curves for normal ears shown in the present paper.

In 1902 Wien[3] published the results of his researches in which he used different types of receivers. The difficulty with these, as with earlier results which were obtained with telephone receivers placed against the ear, was that the ear-characteristics were masked by those of the receiver. Doubtless, the natural frequencies of Wien's receivers when in contact with the ear were in the region of 1,200 d.v. and we should expect the maxima in his curves to occur in this region, as they do. Furthermore, when receivers are used much above their natural frequencies the response of the diaphragm is of a rather complicated nature which cannot well be taken into account and corrected for.

Rayleigh [4] again attacked the problem of the sensitiveness of the ear

[1] Lord Rayleigh, "On the Minimum Audible Current in The Telephone," Phil. Mag., 38, pp. 285–295, 1894; Scientific Papers, Vol. IV., pp. 109–118.

[2] Loc. cit., 1.

[3] M. Wien, "Über die Empfindlichkeit des menschlichen Ohnes für Töne verschiedener Höhe," Pflüger's Arch., 97, p. 1, 1903; Physik. Zs., 4, pp. 69–74, 1902; Wincklemann's Handbuch der Physik, Akoustik, p. 248.

[4] Lord Rayleigh, "On the Relation of Sensitiveness of the Ear to Pitch, investigated by a New Method," Phil. Mag., Vol. 14, ser. 6, pp. 596–604, 1907.

by an entirely different method which depended upon the use of the principle of dynamical similarity.[1] Although his results extended from 85 to 512 d.v. they are of considerable interest in that the variation between these two frequencies was much less than that found by Wien. This difference is probably entirely accounted for by the fact that Wien was not able to correct for the receiver-characteristics. The present data agree with Rayleigh's, in the manner shown by the two curves in Fig. 1. The ordinates are arbritary units of condensations in the case of Rayleigh's data and arbitrary units of current through a receiver tuned to 5,215 d.v. in the case of the present data. The present results are for a particular ear, while Rayleigh's are a mean of several tests on different people. The differences between the two curves are easily explained by the fact that the present data are threshold values while Rayleigh's are "just above" the threshold. Then too, fatigue-effects were completely eliminated in the data taken by the writer.

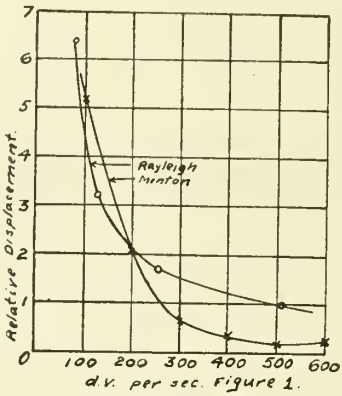


Fig. 1.

Recently Kranz[2] has published results on the sensitiveness of normal ears. In these tests he made use of the thermophone.[3] While this device has no resonance of the ordinary type, it does not give sufficient sound intensity for the purposes of these tests on normal and abnormal ears.

Seashore, Dean and Bunch [4] have carried out extensive tests on normal and abnormal ears by means of their audiometer and an ordinary telephone receiver. However, in the region between 500 and 3,500 d.v. they have been unable to decrease the current in the receiver below the threshold value. For this reason their work is not of importance from the viewpoint of sensitiveness of the ear at various frequencies. Their work is of a clinical nature and is designed to assist in devising an apparatus for the diagnosis of deafness.

The present work, then, was undertaken with the hope of avoiding difficulties encountered by other investigators and, therefore, with the

[1] Lord Rayleigh, Theory of Sound, Vol. II. (§§ 381).

[2] F. W. Kranz, "Minimum Sound Energy for Audition," PHYSICAL REVIEW, p. 384, March 1921.

[3] H. D. Arnold and J. B. Crandall, Thermo-phone, PHYSICAL REVIEW, Vol. 10, pp. 22–38, 1917.

[4] Seashore, Dean and Bunch, "The Audiometer in the Otological Clinic," Am. Otological Soc., Vol. 15, Part II., pp. 36–60, 1920.

hope of securing more trustworthy data on normal and abnormal ears tested over the region of frequencies which is important for speech and for musical sounds.

II. Experimental Procedure.

The present method of testing the sensitivity of the ear, or the degree deafness, consists in determining the minimum audible current, produced by an audion oscillator, at various frequencies through a telephone receiver tuned to a natural period of 5,215 d.v. With these current-readings and with the electrical and vibrational characteristics of the receiver determined by standard impedance analysis,[1] the vibrational energy at the various frequencies of the receiver diaphragm may be calculated. The sensitivity of the ear may be defined as the reciprocal of the vibrational energy of the receiver. This energy can be calculated with considerable certainty provided the receiver is not used above its natural period.

Figure 2 shows a diagram of the testing circuit[2] which has been used

[1] Numerous articles by Kennelly and his co-workers are published in Am. Acad. of Arts and Science, Proc. Am. Phil. Soc., and in the Proc. Inst. Radio Engineers.

The velocity, v, of the receiver diaphragm can be calculated from the following formula which has been used frequently in telephone receiver theory:

$$v = \frac{\omega_0 \sqrt{Z_m r} \sqrt{X_d^2 + (R_d - R_0)^2}\, i}{\sqrt{r^2 + \left(m\omega - \frac{s}{\omega}\right)^2} \sqrt{X_{df0}^2 + (R_{df0} - R_0)^2}}.$$

where $\omega_0 = 2\pi f_0$; f_0 = the natural frequency of the diaphragm.
$\omega = 2\pi f$; f = the frequency (d.v.).
Z_m = maximum motional impedance.
r = mechanical resistance.
m = effective mass of the diaphragm.
s = elastic coefficient.
X_d = damped reactance (variable frequency).
R_d = damped resistance (variable frequency).
X_{df_0} = damped reactance at the natural frequency.
R_{df_0} = damped resistance at the natural frequency.
R_0 = direct current resistance.
i = the minimum audible current.

All these quantities should be expressed in c.g.s. units in order to have the velocity expressed in cm. per second.

The displacement of the diaphragm at various frequencies is given by the equation $x = v/\omega$. The effective mass of the diaphragm (it is considered that the diaphragm curvature is a (cosine)^2 curve) in the case of the high natural period receiver was calculated to be 0.375 gram. The velocity, v, calculated as above, is that of this effective mass (.375 gram) of the diaphragm. The effective vibrational energy of the diaphragm is then given by $1/2mv^2$. The sensitivity, then, is taken to be, in the present work, the reciprocal of this minimum vibrational energy.

[2] This method of measuring the minimum audible current has been used in the past by the Western Electric Co. It was also used and published by E. W. Washburn, "The Determination of the Audibility Current of a Telephone Receiver with the Aid of a Wheatstone Bridge," Proc. Inst. Radio Engineers, pp. 99–109, Vol. 6, 1918.

in this work. The receiver, R, is held against the ear with a constant force by means of a light head band. The oscillator is set for a definite frequency and the current flows through the bridge circuit composed of

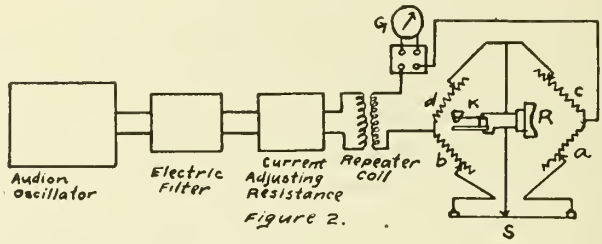


Fig. 2.

non-inductive resistances and the receiver. The resistances c and d are held constant while a, b and the slide wire, S, are adjusted for the threshold values of the minimum audible current. The key, K, is provided so that the patient may operate it intermittently and thus avoid fatigue-effects completely. The minimum audible current can be calculated from well-known formulæ when the values of a, b, c, d, S, the impedance of the receiver, R, and the current through the galvanometer, G, are known.

Two types of curves are shown in the present paper. The first type shows how much current is required for the patient to hear as compared with that required by the ear which had been selected as a normal reference ear. These curves of relative receiver-currents at the various frequencies were taken with the aid of a small receiver placed on a light head band which was of a standard type. The second type of curves shown gives the absolute sensitivity of the ear at the various frequencies. These curves were obtained from those of the first type together with the absolute sensitivity curve of the normal reference ear. This last curve was determined by means of a special telephone receiver tuned to a natural period of 5,215 d.v. The electrical and vibrational characteristics of this special receiver were determined by impedance analysis, and the energy at the various frequencies of the diaphragm was calculated from a formula well known in receiver-theory.

As Rayleigh has pointed out,[1] the resonance of the external auditory canal is materially altered by placing a receiver against the ear. However, tests which have been made show that the maxima of sensitivity for the normal reference-ear (Fig. 3) come at the same positions when the external canal is filled by a soft rubber plug with a small hole through it which connects the drum to the receiver by a small air column. Thus

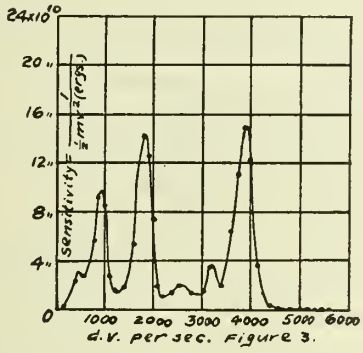
[1] Loc. cit., 4, p. 598.

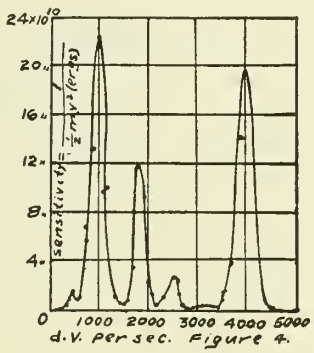
it is fairly certain that, as far as the present tests go, it is not so much in the introduction of resonance in the external ear as in the elimination of such a possible resonance that objection might be raised. The answer to such an objection is that the curves represent the vibratory characteristics of the ear itself, excluding possible air-chamber resonance. This is precisely what is desired in a study of the nature attempted here.

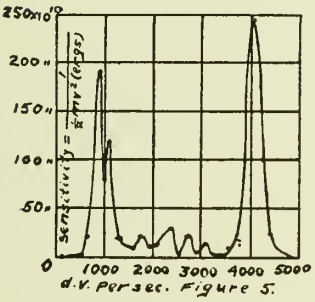
No question can be raised, I think, as to the accuracy of the results herewith reported. Tests made on normal ears over a period of two years check on the average to within about five per cent. Tests on patients, especially on some children as young as five years, have been checked from time to time to an altogether surprising degree.

III. Experimental Results.

Sensitivity of Normal Ears.—Figures 3, 4, 5 and 6 represent the variations that are found among normal ears; that is, ears in which no known







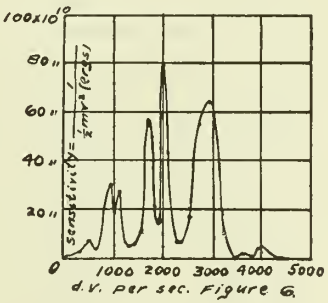


Fig. 3. Fig. 4.
Fig. 5. Fig. 6.

physiological defects exist. The first two curves are the right and left ears of a person 34 years old, the curves in Fig. 5 and 6 are for different persons 23 years old. As already stated, the ordinates represent the

reciprocal of the vibrational energy of the receiver diaphragm whose natural period was 5,215 d.v. The ordinates are probably proportional to sound energy, but more will be said on this phase of the subject later. The total sound energy produced by the diaphragm is probably not more than two per cent. of the vibrational energy.

The curves are seen to have distinct maxima which resemble in all respects the resonant frequencies of coupled mechanical or electrical systems. There are several maxima of much smaller magnitude in each of the curves. These curves have been checked from time to time, so that the smaller maxima are unquestionably present and are not due to observational errors.

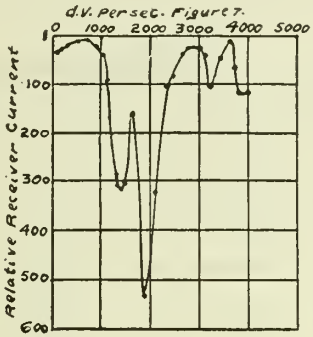
At the threshold of audition, then, there exists a wide variation among normal ears and each ear possesses well defined maxima at particular frequencies. We may refer to these maxima as resonant frequencies for they show definitely that from a mechanical point of view we may think of the ear as a whole as a complex coupled vibratory system. A mechanical system of this nature possesses well-defined resonant frequencies whose positions and magnitudes are determined by the various inertial, elastic, dissipational and coupling coefficients. *The normal ear may unquestionably be thought of in exactly the same way, the various air cavities of the ear being considered as parts of the system.*

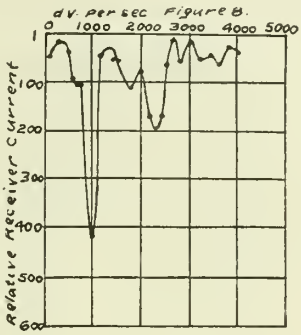
Sensitivity of Abnormal Ears; Middle Ear Deafness.—The six curves shown in Figs. 7 to 12 inclusive are typical examples of those which are obtained for middle ear defects. These curves are comparisons with the normal reference ear (Fig. 3) which was selected for this purpose since it was about an average of the normal ears. In studying these comparative curves one should keep in mind the sensitivity curve for the reference ear and should also bear in mind that these curves are for the threshold of audition only. If the sound intensity is proportional to the vibrational energy of the diaphragm, then the squares of these relative receiver currents give a direct comparison of the sound intensity just necessary for audition for abnormal ears compared with normal ears.

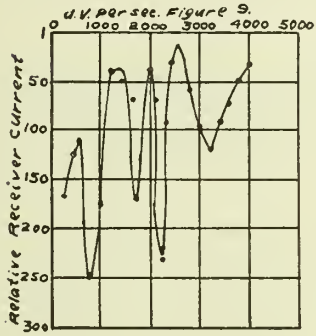
Figure 7 gives the curve for an ear having an abnormally thin drum membrane surrounding the tip of the maleus where it is attached to the center of the drum. Figure 8 is for an ear whose drum is indrawn from its normal position until the tip of the maleus is touching the rear wall of the middle ear cavity. Figures 9 to 12 inclusive show curves for different patients whose defects are the same and is described by the word "otosclerosis" used by the medical profession. This lesion is often described as "fixation of the stapes" of the middle ear.

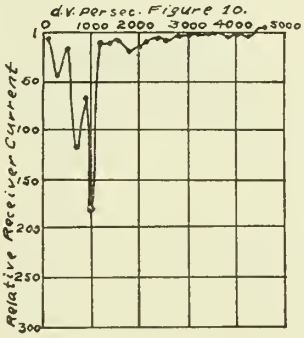
All six of these curves for middle ear deafness show interesting varia-

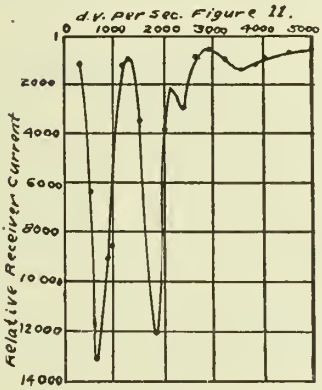
tions that exist in the degree of hearing possessed by individuals. Generally speaking, the depression below normal is greatest at the lower frequencies and the hearing becomes more nearly normal with increasing frequencies. There is, therefore, an increase in the elastic factors of the











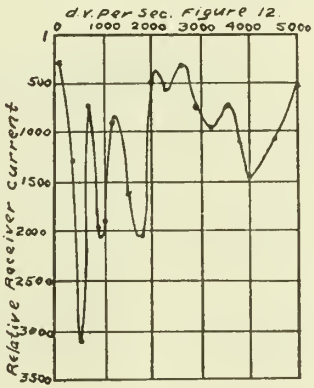
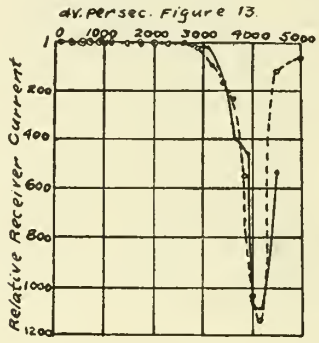
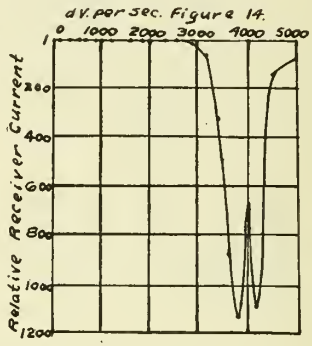
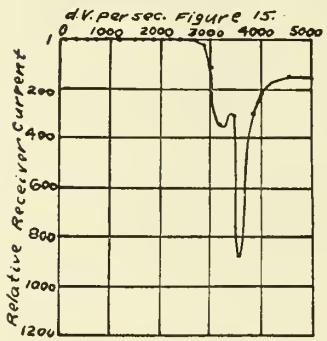


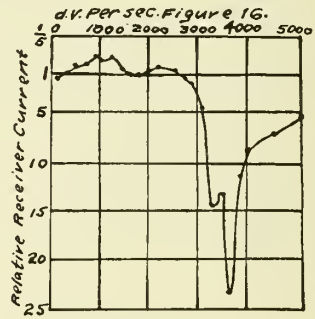
Fig. 7. Fig. 8.
Fig. 9. Fig. 10.
Fig. 11. Fig. 12.

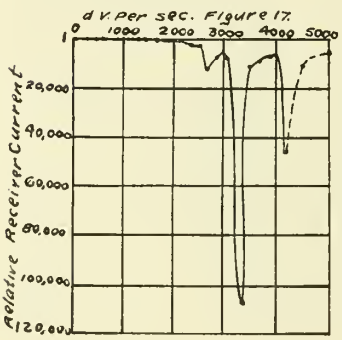
ear considered as a vibrational system. Other physical changes take place also for there is usually a depression in hearing at all frequencies as the curves show. The greatest depressions usually occur at frequencies corresponding to those of the maxima shown in figure 3; namely, from 700 to 1,000, 1,500 to 2,200 and from 3,500 to 4,000 d.v. So that sen-











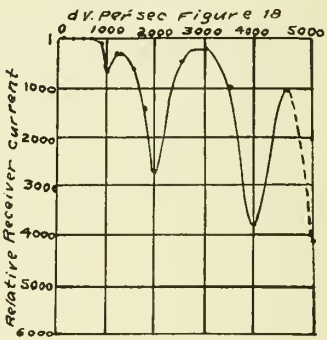


Fig. 13. Fig. 14.
Fig. 15. Fig. 16.
Fig. 17. Fig. 18.

sitivity curves for ears with middle ear defects are much alike among themselves and quite different from those obtained for normal ears.

Attention might be drawn to the sharp depression at 2,200 d.v. in Fig. 9. It was not expected, in view of the normal curve shown in Fig. 3, that this particular decrease in hearing would occur at this frequency. Near the threshold of audition the patient complained of the tone being quite noticeably impure. This did not occur at any of the other frequencies even though the depressions were large. This phenomenon was due to the presence of an internal-ear or nerve lesion which produced in the ear a subjective ringing (tinitus) whose pitch was approximately 2,200 d.v. For a loud receiver tone the patient was not conscious of the tinitus but for a weak tone the intensity of the subjective and objective tones was approximately equal and the patient was quite conscious of the effect produced by the existence of the two tones. So that superimposed upon the middle ear trouble is this internal ear or nerve lesion. The practical application of such information is at once apparent.

Internal Ear or Nerve Deafness.—The group of curves shown in Figs. 13 to 18 inclusive are for different cases of what is called "nerve deafness" by the medical profession. Figs. 13 and 14 are for the left and right ear, respectively, of one patient. Figs. 15 and 16 are for the left and right ear, respectively, of another patient. Figs. 17 and 18 are for different patients.

The dotted curve shown in Fig. 13 was taken about six months after the solid curve was obtained. The two curves are sufficiently alike to make it possible to say that no appreciable changes in the degree of hearing or in the region of the ear affected had occurred during the period of six months. The trustworthiness of the results is at once evident.

The characteristic of the type of nerve deafness which these curves represent is that the sensitiveness is normal at all the lower frequencies and starting at some definite frequency and including all higher ones the degree of hearing is seriously decreased. Thus, the nature of the lesion is such that it is confined to definite frequency limits. Over this confined frequency region, however, the sensitiveness decreases uniformly, reaching minima of sensitivity and then gradually increasing again. In other words, *there is no discontinuity between the affected and the unaffected region.* The location of the lesion in the ear for defects of these types could not be in the middle ear mechanism nor in the drum membrane, for, if such were the case, there would be obtained the types of curves shown in the group of six curves given in Figs. 7 to 12 inclusive. Thus, for these particular curves corresponding to nerve-deafness the vibratory mechanism of the middle ear is in normal condition. The lesion is con-

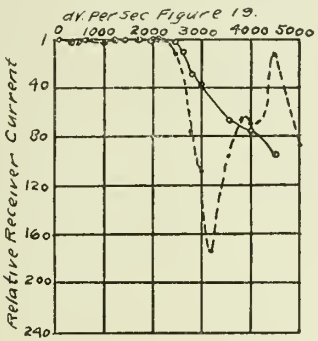
fined to the internal ear mechanism, or in the nerves, including their endings. Since the depressions in Figs. 13 and 14 are so nearly alike in position and magnitude, the question naturally arises as to whether the lesion might not be located at the center of perception itself. It is fairly certain that the question can be answered in the negative for numerous curves for cases of nerve deafness have been taken and practically all of them show that the disease has not affected both ears alike in magnitude and in many cases only one ear has been thus affected. In the example cited above, the agreement in magnitude of the depressions is to be looked upon merely as a coincidence, or that the disease has affected both ears alike. The depressions shown in Figs. 15 and 16 are very likely due to infection from diseased tonsils, but in the present article the medical side of the subject is not considered. Those interested in this phase of the subject may refer to a previous paper by Dr. J. Gordon Wilson and the writer.[1] It is of much theoretical importance, and is indeed surprising, that so great deafness, as for example that shown in Fig. 17, can exist at some frequencies and no deficiency at all appear at the lower ones. In passing it is important to state that with the exception of the last example (Fig. 18) there is not observable a very serious insensitiveness to speech sounds as used in ordinary conversation. The most important region for speech sounds is certainly below 2,000 d.v.

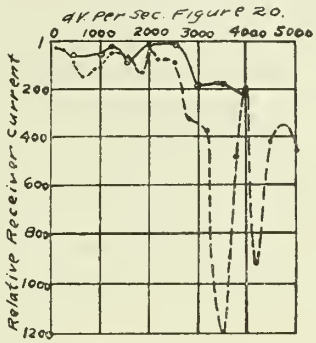
Time Development of Nerve Deafness.—The group of curves corresponding to nerve deafness, to which attention has just been called, show the different stages in the development of this type of deafness. The curves given in Figs. 13 and 14 and in 15 and 16 are for people about twenty-eight years old, while Fig. 17 is for a person about forty-five years old and Fig. 18 is for a person about sixty years of age. This type of deafness, then, becomes more acute and progresses toward the lower frequencies with time. To confirm this view, the curves shown in Figs. 19 and 20 are given. The time interval between the upper and lower curves in Fig. 19 was about eight months, whereas the time interval between the upper and lower curves in Fig. 20 was about thirteen months. The former curves for a case of nerve deafness in a person twenty-seven years of age are alike in sensitiveness at the lower frequencies but unlike at the higher frequencies. The latter curves (Fig. 20) are for a case of both middle and internal ear troubles and during the period of thirteen months a very serious increase has occurred in the extent and magnitude of the deafness for both the middle and internal ears.

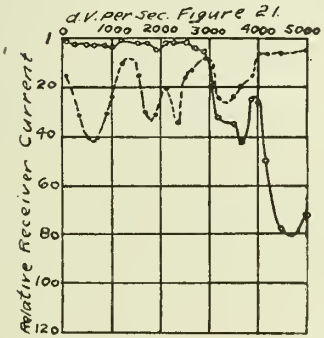
Special Cases and Combinational Defects.—Fig. 21 is interesting in

[1] John P. Minton and J. Gordon Wilson, "The Sensitivity of Normal and Defective Ears for Tones of Various Frequencies," Proc. Institute of Medicine of Chicago, 1921.

that it shows that the type of deafness may be quite different for the two ears of the same patient. The curve marked with the circles is for the ear having an internal ear or so-called "nerve" lesion while the one indicated by the dots is a typical curve for middle ear deafness. The "nerve" lesion is probably traceable to nose and throat infection.







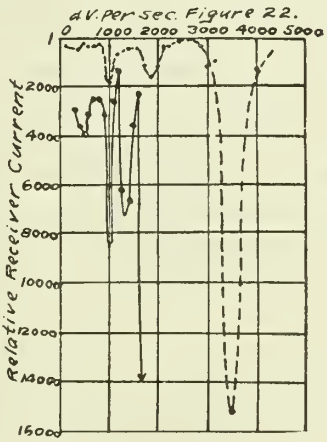


Fig. 19. Fig. 20.
Fig. 21. Fig. 22.

Fig. 20 has already been referred to as representing a combination of middle and internal ear lesions. The curve drawn through the circles indicates internal ear trouble which apparently includes the whole range tested. There is also a suggestion of middle ear trouble in the upper curve, but the lower curve clearly indicates the presence of both a middle and internal ear lesion.

The curves shown in Fig. 22 are quite interesting; the upper one being for the left ear while the lower one is for the right ear of the same patient. The drum membrane, ossicle bones, and tensor and tympanic muscles

are absent in the left ear. Hence, the sensitiveness of the ear due to the sympathic vibrations of these absent members is gone and, therefore, there are three maxima of depression in hearing relative to the normal reference ear (Fig. 3). It is significant that the depressions come exactly in the same localities in which the peaks occur in the normal reference ear. These absent members are, then, almost certainly responsible for the presence of the maxima of sensitivity in normal ears. The large depression below normal at 3,500 d.v. is most probably due to a combination of both middle and internal ear trouble. There is evidently here a true partial nerve deafness for at 2,600 d.v. the hearing was practically normal and from vibrational or mechanical defects alone we could hardly expect such large depressions in hearing on both sides of 2,600 d.v.

The right ear, shown by the lower curve, has the drum membrane and the middle ear mechanism present. Deafness is much more marked in this ear than in the left one. Bone conduction and, therefore, the hearing due to the internal ear and auditory nerves, as tested by length of time the patient could hear vibrating tuning forks placed against the mastoid bone, was equivalent to that of a normal ear up to about 1,200 d.v. or perhaps somewhat higher. Thus the presence of the drum membrane, ossicle bones, stapes, etc., in the middle ear are a hindrance in this case to good hearing rather than an aid to it. Between 1,600 and 1,700 d.v. something amounting to a discontinuity has occurred. The relative receiver current was made 75,000 at 1,700 d.v. and nothing whatever could be perceived. No tones above 1,600 d.v. were heard although the vibrational energy of the receiver diaphragm was maintained at about 5×10^9 times as large a value as is required for audition by normal ears. Thus, we have here a case of what is probably total deafness due to a lesion lying within the nerves including their endings. This curve, and others like it, bring out as clearly as one could wish the sharp distinction between vibrational and true nerve deafness.

IV. Theoretical Aspects of the Present Data.

There has been proposed no theory of the mechanism of audition that has been fully accepted by the various groups of men interested in this field. Helmholtz's[1] basilar membrane resonance theory of the manner in which the ear may be thought of as functioning has not been accepted and is meeting with more and more opposition as further data are collected. Nevertheless, his central idea of the analysis of sounds into the various simple harmonic waves of which they are composed has remained as a fundamental proposition in thinking of the phenomena of audition.

[1] Helmholtz, Tone Sensations.

Shambaugh [1] has rejected Helmholtz's theory and has substituted for it a similar one based on the tectorial membrane vibrating in the manner postulated by Helmholtz for the basilar membrane. The objections urged against Helmholtz's theory may be urged even more strongly against the tectorial membrane theory. Wrightson and Keith [2] in their coöperative study of the ear have rejected the resonance theories of audition and have substituted for them a non-resonant theory of the action of the ear as a whole. It appears, however, from a recent discussion [3] of this theory by the members of the Royal Society of Medicine that there are numerous objections to the Wrightson-Keith theory. Other theories of audition [4] have been proposed, but they will not be referred to here inasmuch as they have not survived the criticism brought against them. The question arises, what bearing do the data reported in the present paper have upon existing theories of audition and do they suggest any modification in these theories?

The general answer to these questions is that this work does show quite definitely in some respects at least how the ear functions. In the first place, it functions as though it were a complex vibratory system, consisting of the drum membrane, the chain of ossicle bones, the tympanic muscles, the internal ear and finally the external and middle ear cavities. The response of this system as measured by the sensitiveness of the ear at various frequencies is exactly of the type that is obtained for an ordinary coupled mechanical system. The resonant frequencies of such a system occur at places controlled by the coefficients which define the system and no resonant frequency can be assigned to any one member of it.

Second, the curves taken on patients who have the drum membrane and the middle ear mechanism absent seems to suggest that the internal ear itself has well-defined resonant frequencies which are located at different places from those of normal ears. A further study of ears of this nature will be of much fundamental importance and it seems best to withold further comments on the vibratory nature of the internal ear until more data are available.

In addition to this mechanical-vibratory functioning of the ear there is a second important mode of operation as the data amply show. In the section on experimental results attention was called to the extremely

[1] George E. Shambaugh, The Laryngoscope, July, 1909, Annals of Otology, Sept., 1910, Dec., 1910.

[2] Wrightson-Keith, An Analytical Mechanism of the Internal Ear.

[3] Royal Soc. Medicine; Section on Otology, discussion March 21, 1919; also The Journal of Laryngology and Otology, Feb., 1921, Vol. 36, No. 2.

[4] Bonnier: Journal de Physique, p. 578, 1906, Theories de L'Audition.

Stefanni: Il Nuovo Cimento, Vol. 61, 1915, La Percezione der Suoni.

sudden and surprisingly large variations in the degree of hearing for the cases of internal ear troubles. Such large variations would not be observed for defects of a purely vibratory nature. The deficiency in hearing due to these internal ear lesions extends over bands of frequency, that is, over a series of consecutive frequencies which cover a range of from one hundred or so double vibrations to as much as several thousand vibrations. In some cases the degree of hearing is equivalent to normal up to about 1,300 d.v. and then within one hundred d.v. it may be so greatly depressed as to amount to total deafness for all the higher frequencies. Again, the hearing may be greatly depressed and then for a small range of frequencies be practically equal to normal, and then with increasing frequency it may suddenly decrease to a very low value. These and other data show, first, that the internal ear is laid out in a linear manner. That is, that part of the internal ear which produces the sensation of low frequency notes is in one section of the ear and the adjacent section produces the sensation of a somewhat higher group of tones. Each succeeding section produces in turn the sensation of higher and higher notes. This view corresponds to that first put forth by Helmholtz and is also in agreement with the present ideas held by otologists. This view is further confirmed by the fact that in advanced stages of "fixation of the stapes" the disease enters the internal ear and affects first the high frequency sounds. This suggests that the basal part of the internal ear responds to the high frequency sounds, while the sections further and further removed from the basal part respond to lower and lower frequencies. Now, in a purely coupled vibratory system it is impossible to greatly affect one member without affecting the response of the system as a whole at all frequencies. For these reasons such defects as have just been described can not be due to middle ear trouble, but are probably due to those parts of the internal ear that have to do with one frequency or with a very narrow group of frequencies. That is, these defects are due either to the fibers of the basilar membrane or to the nerves, including their endings. The extremely sudden depressions in hearing, amounting in many cases to total deafness, are certainly cases of nerve trouble. The gradual depression in hearing for the higher frequencies cannot be called nerve deafness without considering the subject further. This discussion leads us to the rôle played by the basilar membrane.

Let us assume that the shortest fibers of the basilar membrane respond best to the highest frequencies, that the somewhat longer fibers respond best to somewhat lower frequencies, and so on until we arrive at the longest fibers which respond best to tones of the lowest frequencies.

Since the length of the longest fibers is but two or three times that of the shortest ones, in order that the assumption may hold, it seems necessary that the tension in the fibers increase rather rapidly with the decrease in their length. If this be true, then, for purely mechanical reasons the fibers may be expected to give way first over all the high frequency region because of the comparatively large tension in the fibers which cover this region. Hence, we may expect the sensitivity for tones of the highest frequencies to be lost sooner than for tones of the lowest frequencies. We may also expect that, as time goes on, the disturbance will travel in the direction of lower frequencies and become more and more acute for the higher ones. For this sort of a condition, which is not of the nature of a disease, we should expect to obtain the type of curves shown in Figs. 13 to 18 inclusive. From the point of view here considered, then, this type of so-called "nerve-deafness" is not nerve-deafness at all, but is rather a special type of vibratory deafness caused by the peculiar construction of the basilar membrane. True nerve-deafness would show itself by a sudden depression in hearing amounting in some cases to a total discontinuity in the curves. It should be borne in mind, however, that much additional data must be collected before such a theory can be very positively advanced.

The bearing of the foregoing experiments upon the Helmholtz theory of pitch perception is most clearly seen from a consideration of Fig. 17. It will be seen from a glance at this figure that at a frequency of 3,300 d.v. the current required to excite audition was about 110,000 times that required by the normal ear, while in the whole frequency region below 1,200 d.v. the patient's hearing was normal. The relative *energies* corresponding to the current-ratio, 1 to 110,000, is approximately 1 to 10 billion. In other words, it was possible in the case of this patient to apply in the frequency region of 3,300 d.v. an energy 10 billion times as much as corresponds to normal hearing at this frequency without stimulating in the slightest degree the sensation of hearing in the region below 1,200 d.v. where the patient's hearing was practically normal. Now in the Helmholtz theory, pitch perception is due to the coincidence of the impressed frequency with the natural frequency of the fibers of varying length and tension which constitute the basilar membrane. It is, however, extremely difficult to see how a mechanical system such as that represented by the basilar membrane with its fibers and attached Corti's arches could possibly receive ten billion times the normal energy at a given frequency like 3,300 d.v. without imparting as much as a billionth of that energy to the adjacent fibers which corresponds to vibration frequencies below 1,200 d.v. If these latter fibers had in this

case been thus forced into response with a billionth or even a hundred billionth of the incident energy the patient would have had the sensation of hearing in the region below 1,200 d.v. as can be seen easily by a reference to Fig. 3. If these considerations are fatal to the Helmholtz theory, there appears to be no alternative at present but to make pitch perception a property of the nerves themselves, including their endings, without attempting to find a mechanical explanation. This amounts to nothing more than the assertion of our inability at present to obtain a satisfactory mechanical basis for pitch perception.

In conclusion, the writer wishes to take advantage of this opportunity to express his appreciation for the continued interest and the very helpful suggestions received from Professors Millikan and Lunn throughout this work.

RYERSON PHYSICAL LABORATORY,
UNIVERSITY OF CHICAGO,
July, 1921.

THE EFFECT OF OXYGEN AND HYDROGEN ON THE EMISSION OF ELECTRONS FROM HOT PLATINUM.

By Laurice L. Lockrow.

Synopsis.

Thermionic Emission from a Platinum Filament.—Previous observers have reported such conflicting results as to the effect of gases on the emission that a series of 20 tests were carried out by the author to determine the cause of these discrepancies. A tube with a long cylinder surrounding a V-shaped filament was found to give results more free from saturation difficulties, but even with it complete saturation could not be obtained, due perhaps to the presence of heavy negative ions. (1) *The effect of oxygen and air* on the emission was found to be to decrease it slightly, in agreement with the observations of Richardson, H. A. Wilson and others. This effect is temporary and is not due to the formation of heavy ions; and while it may accompany the formation of an oxide of platinum, no evidence for this was obtained. (2) *The effect of hydrogen* on the emission from pure platinum is probably nil. For in those cases in which the hydrogen causes a "permanent increase," that is an increase which remains after the removal of the hydrogen, the author's tests indicate that the effect is due to grease or oil vapor, although the hydrogen may hasten the action; and the large "temporary increase" usually observed when hydrogen is admitted is found to disappear upon heating the filament a long time in air and hydrogen, and hence is probably due to the action of hydrogen not on the platinum itself but on impurities contained in the filament. (3) *Richardson's constants for pure platinum* were found to be: $A = 9{,}900$; $b = 52{,}000$. These values are lower than those obtained by others and are subject to errors inherent in the resistance method of measuring temperatures. (4) *The thermionic work function for platinum* computed from the value of b comes out 4.46 volts as compared with 4.80 volts obtained by Koppius for the corresponding photo-electric function.

CONSIDERABLE material dealing with the emission of electricity from hot bodies has been published, so the writer will not go into a discussion of the general aspect of the problem in hand. Those to whom the subject is not familiar are referred to the several sources of information mentioned below.[1]

The effect on the emission of changing the filament temperature and the anode voltage has been well determined. The effect of gases has not been as well worked out. The writer hopes to point out in this paper several ideas in connection with the effect of gases on the emission of electrons from hot platinum.

From the results of experiments published in 1903, Dr. H. A. Wilson[2]

[1] "The Emission of Electricity from Hot Bodies," O. W. Richardson. "The Electrical Properties of Flames and Hot Bodies," H. A. Wilson.

[2] Phil. Trans., A, 202–243–1903.

concluded that the negative leak of electricity from a hot platinum wire in air, nitrogen or water vapor is independent of the gas pressure unless ionization by collision occurs and is approximately the same as the negative leak from the wire in a good vacuum. He also concluded that the negative leak in hydrogen is much larger than that in air or in a vacuum and that at low pressures it is very nearly proportional to the pressure of the hydrogen. O. W. Richardson [2] found that in certain cases the current in hydrogen was independent of the pressure over the range of 1 to 0.001 mm. Wilson later found [1] that in certain cases the leak was independent of the pressure over a range of 200 to 0.001 mm. He also found the leak with new wires to be a function of the gas pressure, but after the wires had been subjected to considerable heating in hydrogen the leak usually became independent of the pressure.

Langmuir [2] concluded from his experiments on tungsten that hydrogen permanently lowered the current, especially at low temperatures. He suggested that "oxygen would have a similar effect on the thermionic current from platinum that nitrogen has on tungsten. In other words, the oxygen would cut the thermionic current down to a value lower than the normal vacuum current (by the formation of an oxide). Hydrogen would reduce the oxide and allow the normal vacuum current to flow. Of course it is quite possible although not probable, that some gases may increase the thermionic current instead of decreasing it."

Due to these conflicting ideas the problem was again taken up. It was found that oxygen decreased the leak slightly and that after the platinum had been purified by heating for a long time, alternately in hydrogen and air, the hydrogen had no effect on the current. The results of these experiments led to an explanation of the results obtained in the previous cases.

Apparatus and Methods.

In the experiments two types of tubes were used, designated as the old tube and the new tube. The old tube was made with two filaments hung vertically as shown in Fig. 1. By using two filaments both could be freed from gas by connecting in series and heating before a test. During a test the one was heated, furnishing the electrons and the other was cold, serving only as the anode. All filaments were of "chemically pure platinum," 0.25 mm. diameter and 8 to 10 cm. long.

The old tube required a fairly high voltage for saturation and ionization by collision occurred so as to hide the true effect of the gas. No difficulty from gases occluded in the metal parts was experienced. Ac-

[1] Phil. Trans., A, 208–247–1908.

[2] Phys. Rev. 2–450–1913.

cordingly the new tube was made with a cylinder of platinum surrounding a V-shaped filament. The cylinder was about one cm. in diameter and 4 cm. long. The tube was arranged so as to minimize the leakage of current over the surface of the glass.

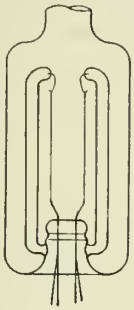


Fig. 1.

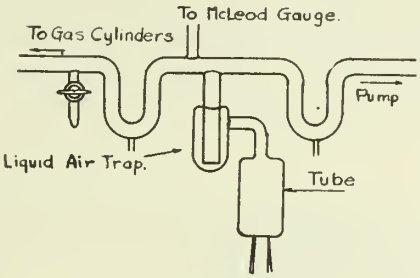


Fig. 2.

The apparatus was arranged as in Fig. 2. The system was exhausted by a Langmuir condensation pump backed by the usual oil pump. The pump could be cut off from the apparatus by a mercury column. The pressure was measured by a McLeod guage reading to about 0.00001 mm. The tube was separated from the remainder of the apparatus by a liquid air trap, and was placed as close to the pump as possible. In the first series of tests, the oxygen and hydrogen were stored in glass cylinders and were admitted to the apparatus through capillary tubes having stopcocks arranged to admit only a small amount of gas each time. The hydrogen was prepared from a solution of sodium hydroxide acting on aluminum. The oxygen was obtained from an "Oxone" generator. Both gases were purified by bubbling through a strong solution of potassium hydroxide and were dried over phosphorus pentoxide. A spectrum of a sample of the hydrogen excited electrically by a condenser discharge showed faint traces of nitrogen but no other impurity. A stopcock was provided to admit air. In the second series of tests hydrogen and air were the gases used. The cylinders were replaced by an electrically heated platinum tube by means of which hydrogen from a Kipp generator could be diffused into the apparatus. The air was admitted as before. A second mercury column was arranged to cut off the stopcock and the gas supply apparatus from the tube.

The filament temperatures were measured by the resistance method with the help of a Wheatstone bridge as shown in Fig. 3.

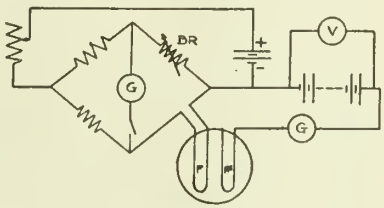


Fig. 3.

The Callender correction formula was used in the calculations. A correction for the cooling at the ends of the filament was made by assuming that 1 cm. of the total length of the filament has half the resistance of every other centimeter of the filament, so that for a total length of 8.4 cm., in the last series of experiments, the effective length was taken as 7.9 cm. The constants needed in the calculations were determined from readings at 0° C., 100° C., and 1066° C.

The thermionic currents were measured by means of a sensitive galvanometer provided with an Ayrton shunt.

Experimental Work.

The experimental work was done in a large number of separate tests. From these, tests were selected as being typical. These are presented in the following material.

Test No. 1.—These early tests were performed with the old type of tube as described before. At the beginning of each test the tube was heated by a small electric furnace placed around it, to a temperature of about 350° C. The filaments connected in series were glowed out and the pumps were operated. The test was not started until the gauge indicated a pressure of about 0.00001 mm. Liquid air or solid carbon dioxide was kept on the liquid air trap.

A typical curve obtained with a new filament is shown in Fig. 4. The

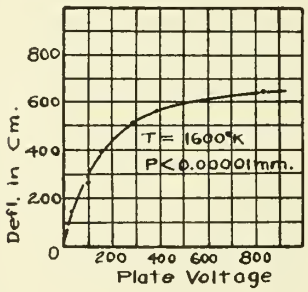


Fig. 4.

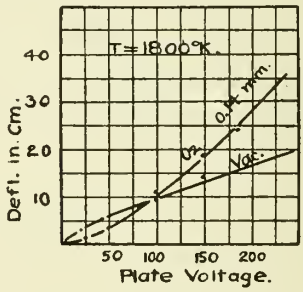


Fig. 5.

galvanometer deflection[1] due to the thermionic current is plotted against the plate voltage. It was found that this type of curve gave good indications as to the action of the tube and so was used throughout the remainder of the tests. In this case the current was large at a low temperature and was not easily saturated. This is characteristic of a new filament. The current decreased rapidly with time. Further heating with the pump operating and again in oxygen at low temperatures reduced the current to a low steady value which could be reproduced.

[1] One cm. deflection 5×10^{-8} ampere.

Test No. 2.—The current in oxygen as compared to that in a good vacuum is shown in Fig. 5.

The gas decreases the current to a small extent when the plate voltage is low. At the higher plate voltages the current is much larger than in a good vacuum. This increase in current is due to ionization by collision. Other tests were made with oxygen at pressures and temperatures respectively of 0.65 mm. and 1700° K., 0.56 mm. and 1830° K. with similar results. In every case the current returned to its initial value on removing the gas.

Test No. 3.—With a filament which had been in use for a time, curves were obtained as in Fig. 6. In a good vacuum the current did not saturate definitely and was a function of the temperature as well as voltage for low voltages at which the space charge relation should hold. This may be due to the presence of heavy charged particles in the emission or to the construction of the tube.

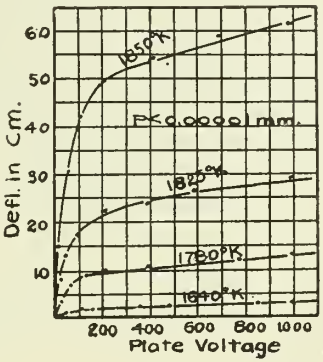


Fig. 6.

In the process of determining Richardson's constants for the above data, it was found that the points representing log $i - \frac{1}{2}$ log T plotted with $1/T$ did not lie on a straight line. However, by drawing a line representing as nearly as possible the coördinates, the following values were obtained:

$$A = 3{,}020,$$
$$b = 46{,}000.$$

Test No. 4.—Hydrogen at 0.55 mm. increased the current by a large amount at a temperature of 1710° K. The galvanometer readings are given below, contrasted with those obtained later in a good vacuum at the same temperature:

Plate Voltage.	Defl. with H_2.	Defl. in Vac.
10 volts	23.5 cm.	1.1 cm.
20	60	2.2
30	580	2.85
40	900	3.55

Further tests at this time with hydrogen gave erratic curves. The currents were large.

Test No. 5.—In hydrogen at 0.55 mm. pressure and at 1720° K. the

current was 14,000 units at 100 volts. Before admitting the hydrogen the current had been 8 units at 1710° K. and with the same voltage. The current did not return to its initial value upon removing the hydrogen. The curves were of about the same shape as before but the currents were much larger and were well saturated with the voltages used. At the higher temperatures the current began to fall off with time. For this "permanent effect" the following values of Richardson's constants were obtained:

$$A = 10^8,$$
$$b = 54{,}000.$$

Test No. 6.—The remaining experiments show that the permanent increase in current after heating the filament in hydrogen was really a secondary effect, and that there was a temporary increase in current which practically disappeared after working with the filament a long time. In these experiments the hydrogen was admitted to the apparatus by diffusion through the hot platinum tube.

The tube was heated and the filaments were heated in air. The tube was pumped out and solid carbon dioxide was put on the liquid air trap. Curves were obtained in hydrogen after heating in it at 0.0055 mm. for half an hour, after heating in it at 0.46 mm. for 5 minutes and again after heating in it at 0.51 mm. for half an hour. The temperature was 1630° K.

In every case the hydrogen caused a temporary increase in current. Upon removing the hydrogen the current dropped to a value comparable with its original value in a vacuum. There was a progressive decrease in the vacuum current throughout the test as is characteristic of a new filament.

Test No. 7.—The filament was heated in hydrogen at a pressure of 3 or 4 mm. at 1130° K. for 65 minutes. The hydrogen temporarily increased the current by a factor of 25 to 30 at low voltages. The currents after heating in the hydrogen are very nearly the same as those before as indicated in the following table:

Voltage.	Deflection of Galvanometer.		
	In Vac. before Heating in H_2	In H_2.	In Vac. after Heating in H_2.
15	0.40	8.7	0.40
30	0.75	18	0.85
160	1.10	33	1.25
120	1.32	64	1.40
200	1.50	220	1.60

Filament temperature 1680° K.

Test No. 8.—Hydrogen at 3 or 4 mm. pressure was allowed to remain in the tube 17 hours with no carbon dioxide or liquid air on the trap. At the end of this time the filament was found to be coated with a black deposit which slowly disappeared when the tube was heated and the filament glowed. Air was then admitted to about 7 mm. pressure.

A permanent effect apparently due to the hydrogen was found after letting the tube stand with hydrogen in it. The current in the hydrogen at 1680° K. was less than the current after pumping out at voltages below 350. The vacuum saturation current was 1,300 times larger than the small current obtained after heating in air for the same temperature. The current in air was somewhat smaller than the usual vacuum current at low voltages.

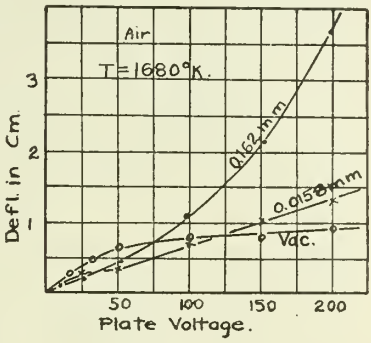


Fig. 7.

Test No. 9.—After heating the filament in air for a short time, the tube was exhausted. Air was admitted again with carbon dioxide on the trap and curves were obtained at pressures of 0.162 mm., 0.0158 mm., and in a good vacuum. These curves are given in Fig. 7.

The current in air was less than in a good vacuum at low voltages at which no appreciable ionization by collision occurs.

Test No. 10.—Hydrogen at 3 or 4 mm. pressure was allowed to stand in the tube for 10 hours with carbon dioxide on the trap. At the end of this time the gas was pumped out and a curve was obtained.

The current after the hydrogen had been removed was the same as before admitting it. That is, hydrogen had no permanent effect on the current when the liquid air trap was maintained at a low temperature.

Test No. 11.—This test was similar to No. 8. The tube was allowed to stand for 43 hours with hydrogen at 1/2 mm. in it. There was no refrigerant on the trap. At the end of this time the filament was found to be dirty in spots. The tube was pumped out. Upon heating the filament a grey deposit resembling finely divided mercury was driven from the filament to the walls of the tube. Upon heating the tube with the pump shut off, a pressure of 0.00097 mm. was recorded.

The hydrogen was again found to give a permanent effect when no refrigerant was used.

Test No. 12.—The apparatus was allowed to stand two days with air in it at atmospheric pressure. The pressure was reduced to 3 or 4 mm. and kept there the third day. All gas was then removed and the

filaments were allowed to stand for two days in the vacuum. The tube was then pumped out. The current was found to be small but it increased rapidly upon heating several minutes. After pumping out again after two hours, a large current was obtained. Heating in air brought the current back to its small value.

Test No. 13.—The tube and air trap were sealed directly to the pump. Mercury was put into the liquid air trap and was heated.

The mercury alone gave no permanent effect.

Test No. 14.—The current was measured and then hydrogen and mercury vapor were admitted, using the same apparatus as in the previous test. The filaments were heated for a short time. Upon pumping out the current was found to be small.

Mercury vapor and hydrogen gave no permanent effect.

Test No. 15.—A tube containing stopcock grease was sealed to the apparatus near the tube. The grease was heated and then after a few minutes the tube was freed from gas. The current was large but decreased slowly at high temperatures.

For the "permanent effect" produced by the grease vapor these values of Richardson's constants were obtained:

$$A = 9.70 \times 10^8,$$
$$b = 58{,}400.$$

Test No. 16.—The previous tests indicated that the permanent effect might even be produced in a good vacuum. To eliminate the permanent effect as far as possible air was admitted to the tube whenever left standing, and the filaments were heated in air for several hours before beginning the tests. The tube itself was also heated. Liquid air was used in these tests and it was not put on the trap until the pressure was down to about 1/2 mm.

The filament was kept at 1,800° K. and hydrogen was admitted in small amounts. The deflections of the galvanometer with 43 volts on the plate were as follows:

Pressure.	Deflection.	Pressure.	Deflection.
0.00001 mm.	1.25 cm.	0.30	1.60
0.0001	1.25	0.36	1.65
0.057	1.40	0.44	1.80
0.09	1.50	0.49	1.90
0.15	1.50	0.69	2.00
0.25	1.60	0.0067	1.80

The slight increase in current in this test may be due to a real effect,

or, more probably, to the inability to maintain constant temperature. At any rate, the increase in current is small.

Test No. 17.—The new type of tube having a cylindrical anode was used in the remainder of the tests. With this type of tube the currents were fairly well saturated with 20 to 25 volts as compared to 100 to 200 volts for the previous type.

The following values of Richardson's constants were obtained with this type of tube after working with it a short time:

In a vacuum	$A = 300$	$b = 46{,}600$,
In hydrogen, $p = 0.0195$ mm.	$A = 1{,}230$	$b = 48{,}000$,
In hydrogen, $p = 0.0014$ mm.	$A = 795$	$b = 48{,}000$.

Test No. 18.—The filament was maintained at constant temperature and hydrogen was admitted to various pressures.[1]

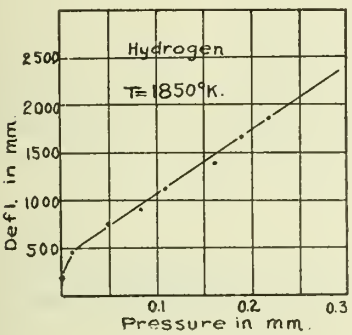


Fig. 8.

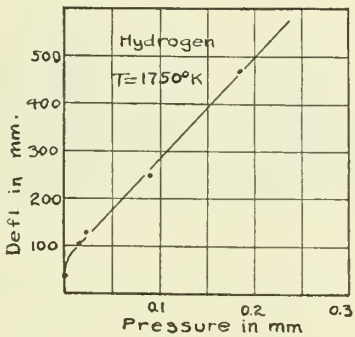


Fig. 9.

The results of the test are shown in Figs. 8 and 9, above. The current in the gas was found to be fairly well saturated as indicated by Fig. 10 below.

The deflection-pressure curves are straight lines except for the lower portion of the curves. These curves show the increase in current to be a linear function of the gas pressure provided the pressure exceeds a minimum value of about 0.01 mm.

The lead-in-wires of this tube were not very heavy and it was thought that there would be less error in temperature measurements with heavier leads. Accordingly the test was stopped, and another tube of the same type but with heavier leads was made.

Test No. 19.—The new tube gave a fairly large current at the start. Hydrogen increased the current by a large factor at first. This increase due to hydrogen fell off with time. The data was as follows:

[1] A change in the galvanometer was made. The new galvanometer gave 6.66×10^{-10} ampere per mm.

Gas.	Temperature.	Deflection.
Vac.	1800° K.	570 mm.
H_2 — 0.078 mm.	1800°	12,000
Vac.	1800°	660
Air.	1800°	———
Vac.	1800°	210
H_2 about 0.1 mm.	1900°	20,000
H_2 about 0.1 mm.	1800°	9,000
Vac.	1800°	300
H_2 1/2 mm.	1900°	15,000
H_2 1/2 mm.	1800°	3,200

The following values were obtained for A and b in a good vacuum:

$$A = 316,$$
$$b = 46{,}000.$$

Test No. 20.—The filament was heated for 5 or 6 hours alternately in air and hydrogen. After this heating the current in a vacuum was the same as in hydrogen within the limits of accuracy of the experiment. The current in air was slightly less than in a vacuum. The currents were well saturated as indicated by the typical curves in Fig. 11.

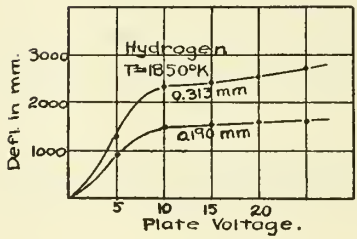


Fig. 10.

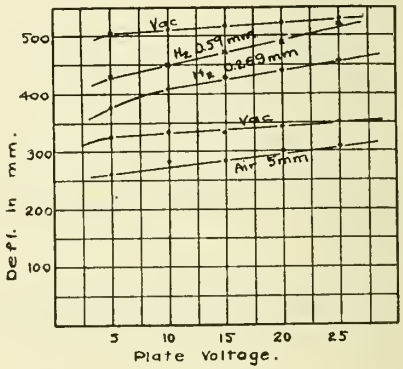


Fig. 11.

A summary of all the readings at 10 and at 15 volts are given in Table I. These voltages were chosen as being the ones at which the readings are typical.

Averages of these readings were made and for these, Richardson's constants were obtained as

$$A = 9{,}910,$$
$$b = 52{,}200.$$

Table I.

Summary of data for Test No. 20.

Temperature 1900° K.

Gas.	Pressure.	Defl. for 10 Volts.	Defl. for 15 Volts.
Vac.		515	525
		475	485
		410	410
			350
		335	340
Air	5 mm.	280	290
		400	410
		355	360
H_2	0.0352 mm.	390	410
	0.0475	450	450
	0.098	470	480
	0.181	425	435
	0.269	410	425
	0.590	450	470

Temperature 1850° K.

Vac.		255	265
		230	235
		210	210
			180
		180	180
Air	5 mm.	140	145
	0.266	175	175
H_2	0.0352 mm.	175	180
	0.0475	245	250
	0.098	240	245
	0.181	195	200
	0.269	195	200
	0.405	150	155
	0.590	235	245
	2	150	160
	3	165	180
	6	170	180
	8	175	180
	14	220	240

TABLE I. (*Continued.*)

Temperature 1800° K.

Gas.	Pressure.	Defl. for 10 Volts.	Defl. for 15 Volts.
Vac.		115	120
		100	105
		90	92
			75
		73	73
Air	5 mm.	70	71
	0.226	74	76
	0.0186	76	77
H_2	0.0352	74	74
	0.0475	100	100
	0.098	104	105
	0.181	92	94
	0.269	90	92
	0.590	115	120

Temperature 1750° K.

Vac.		61.5	63
		54	55
		45	47
			41
		42	43
Air	5 mm.	35	36
	0.226	46.5	47
H_2	0.0352	40	41
	0.0475	50	53
	0.098	51	52
	0.181	46	47
	0.269	44	45
	0.405	36	37
	0.590	58	61.5
	2	35	42
	3	33	34.5
	6	33.5	35.5
	8	39	41
	14	67	74

TABLE I. (*Continued.*)

Temperature 1700° K.

Gas.	Pressure.	Defl. for 10 Volts.	Defl. for 15 Volts.
Vac.		26	27.5
		21	21.5
		17	18
			14
		14	14
Air	5 mm.	12	12
	0.226	15	15.5
	0.0186	13.5	14
H_2	0.0352	12	13
	0.0475	20	20
	0.098	17.5	18.5
	0.181	13.5	15.5
	0.269	13	14
	0.590	25	26
	14	23	27

DISCUSSION AND CONCLUSIONS.

The Normal Vacuum Current. Tests Nos. 1–3–17–19–20.—For convenience, the current in a vacuum after the filament has been heated in air or oxygen long enough to remove any surface impurity such as carbon, is designated the normal vacuum current. The normal vacuum current from a new filament is large and is not readily saturated. With further heating the current decreases and becomes more easily saturated. Heating alternately in hydrogen and oxygen hastens the decrease in current.

After working with the filament for a long time, there is still a difficulty of saturation. With the old type of tube the curves (Fig. 6) are not in accordance with the theoretical space charge curves. Since the voltage across the filament did not exceed 5 volts, it is not likely that the filament drop caused this departure. The failure to follow the space charge relation is probably due to the construction of the tube or the presence of heavy charged particles in the emission. With the new type of tube, the space charge relation could not be studied because the voltage for saturation was but very little larger than the filament drop. The failure to obtain complete saturation remained. With both types of tubes, the lack of complete saturation seems to be due to the presence of heavy charged particles in the emission.

The values of Richardson's constants for the normal vacuum current for filaments which had been used for some time are summarized below:

Test No.	A.	b.
3	3,020	46,000
19	316	46,000
20	9,900	52,000

The last pair of values are the most reliable to take as the values of Richardson's constants for pure platinum as they were obtained from the average of a large number of readings and after the filaments had been used a long time. They are, however, subject to the errors of the method of measuring the temperature and ought not be considered precision measurements. They are worthy of consideration as better than the usual qualitative measurements. Experiments in which the temperatures are measured by optical methods ought to be performed as a check.

From this last value of b, we get the work function, or the potential corresponding to the velocity of an electron necessary to let it escape from the metal as 4.46 volts. This is comparable to the value of 4.80 volts obtained by Koppius [1] as the work function for the photoelectric effect of platinum.

These values of A and b are both lower than those obtained by others. Quoting H. A. Wilson,[2] "For pure platinum in a vacuum or in air at low pressure O. W. Richardson, H. A. Wilson, F. Horton, Deininger and others have all obtained values of Q differing little from 130,000 ($b = Q/2 = 65{,}000$). As to A, however, there is a good deal of doubt, for a small error in the currents leads to a large error in A, and traces of hydrogen or other impurities change A much more than Q. It is probable that A for pure platinum is not much less than 10^8." The temperature scale may be different from that used in the previous experiments, so as to cause the difference in results. In the experiments described here, the effect of hydrogen has been eliminated as a source of error. The impurities which caused the temporary increase of current when hydrogen is admitted, as discussed in subsequent pages, have been eliminated. There may remain, however, other impurities.

The Current in Oxygen and Air. Tests Nos. 2–9–20.—The effect of oxygen was similar to the effect of air in the case of the old type of tube. The current in both cases was smaller in the gas than in the vacuum at the lower voltages. With the higher voltages the current was larger in the gas.

The tests with air in the new type of tube indicate a small decrease in current due to the gas. The tests with the new tube were not confused by ionization by collision and allow a definite conclusion.

[1] PHYS. REV., 17, 395, March, 1921.

[2] "El. Prop. of Flames and Hot Bodies," page 15.

The decrease in current may be due to the formation of an oxide of platinum on the surface, having a smaller emission than the platinum. If there is such an oxide, it is quite volatile because on removing the gas the current returns to its normal value. Langmuir proposed the idea of an oxide in connection with the effect of hydrogen. These experiments indicate that the formation of an oxide does not play a part in the increase of current due to hydrogen. The decrease cannot be ascribed to the formation of heavy negative ions[1] which tend to decrease the current because the current remains fairly well saturated. Heavy ions would not decrease the final current but would make saturation more difficult. The tests are in accordance with the tests made by others as previously mentioned.

The Effects of Hydrogen on the Current. Tests Nos. 4 to 8 Inc., 10 to 20 Inc.—A discussion of the effects of hydrogen is best made by considering the so-called "permanent effect" and the "temporary effect."

The permanent effect was first noted in Test No. 4. From Tests Nos. 6–7–8–10–11–12, the conclusion was drawn that the hydrogen itself does not produce a permanent effect. The permanent effect was due to something which was stopped by the refrigerant on the liquid air trap. Mercury vapor, grease vapor from the stopcocks and oil vapor from the pump were the only substances which could aid in producing the permanent effect. Mercury vapor alone and with hydrogen was found to give no permanent effect. The grease vapor was found to give a permanent effect. The oil vapor was not tested but in view of the results of a subsequent test with benzene, it is probable that it has the same effect as grease vapor. The grease and oil vapor slowly diffuse into the tube and when the filament is heated the vapor is decomposed giving the filament a coating of carbon which increases the current. Upon admitting air this coating is burned off and the current returns to its normal value. Hydrogen is not an essential to the permanent effect because the effect was obtained even with a good vacuum, but it hastens the action by carrying the vapor through the apparatus more rapidly.

The values of Richardson's constants given by the permanent effect and after heating the filament in grease vapor (in the same type of tube) are:

Permanent effect	$A = 10^8$,	$b = 54{,}000$.
Grease vapor	$A = 9.7 \times 10^8$,	$b = 58{,}400$.

These values are comparable and tend to further identify the permanent effect with the effect due to grease vapor.

[1] L. B. Loeb, Phys. Rev., 17, 89, Feb., 1921.

In a test not previously discussed, the filament was coated with a black deposit of carbon by heating in benzene vapor at about 1700° K. for several minutes. The values of Richardson's constants obtained in a vacuum with this carbon deposit were $A = 240{,}000$ and $b = 50{,}700$. These values are not so comparable with those given above, on account of the fact that another type of tube was used. Hydrogen at 0.27 mm. pressure was found to have no effect on the current from the carbon coated filament.

This permanent effect was found by Richardson [2] and later by Wilson [3] but was attributed to hydrogen dissolved in the platinum. The effect is described in the following excerpts from Dr. Wilson's book,[1] Chap. 3:

"In some experiments Richardson found that the leak from a hot platinum wire in hydrogen was independent of the pressure, even when this was reduced to a very small value. The writer found that this is always the case after a wire has been heated in hydrogen at a comparatively high pressure for some time. After this treatment the properties of a wire are completely changed."

"The wire then gives a large thermionic current practically independent of the pressure of the hydrogen from 760 mm. down to less than 0.001 mm."

"If the wire is heated in air or oxygen the large thermionic current immediately disappears. It can also be made to disappear by heating above 1700° C. in a very high vacuum. These facts make it very probable that the hydrogen combines with the wire, forming a very stable compound. This compound must have a very small dissociation pressure. It must also be formed very slowly unless the pressure of the hydrogen is high."

The characteristics of the permanent effect mentioned by Wilson are the same as those in the experiments of the writer. In view of the experiments described, the writer prefers to attribute the effect to grease or oil vapor rather than to hydrogen dissolved in the wire.

When hydrogen is admitted to a tube containing a new filament, there is a very large temporary increase in current and a slight permanent increase. In Test No. 19, the current was temporarily increased by a factor of 20 at 1800° K. with a gas pressure of only 0.078 mm. This increase falls off with continued heating and quite rapidly upon heating successively in air and hydrogen. The filament comes to a state in which the temporary effect is regular and can be reproduced provided the temperature is not raised too high. The increase in current due to the hydrogen is proportional to the pressure of the gas provided the pressure is above a certain minimum value.

With further heating in hydrogen and air at high temperatures, the temporary effect becomes smaller. In Test No. 20, the heating was continued until the effect had disappeared.

The conclusion is that the temporary increase in current when hydrogen is admitted is due to the action of the hydrogen not on platinum but on some impurity in the platinum. Alternate heating of the filament at high temperatures in air and hydrogen reduces the impurities to a state in which they cause no increase in current or frees the filament of them entirely. The latter action is the more likely. Carbon might be one of the impurities, but heating in air would take it from the filament. Then also, hydrogen was found to have no effect on the current from a deposit of carbon. An oxide of a metal, as calcium, for example, might be the impurity. It is known that hydrogen increases the current from calcium oxide. There is one thing to be pointed out: the action is not that of the reduction of an oxide to a metal, giving a larger emission, because as soon as the gas is removed the current returns to its normal value. In the case of the reduction of an oxide, oxygen would have to be present to bring the current back to its normal value.

The opinion had been that the temporary effect was due to hydrogen dissolved in the platinum. From this work it appears that the effect is due to hydrogen dissolved in the impurities in the filament but not in the platinum itself.

Summary.

In closing, the writer wishes to express his sincere thanks to Dr. H. A. Wilson of Rice Institute, Houston, Texas, where this work was done, for his interest in the investigations and for his suggestions and criticisms which have led to the successful accomplishment of this work.

Rice Institute.

THE ELECTRON THEORY OF METALS IN THE LIGHT OF NEW EXPERIMENTAL DATA.

By P. W. Bridgman.

Synopsis.

Deviations from Ohm's Law at High Current Densities of 5×10^6 amp./cm.^{2} have been detected in the case of Au and Ag foils, of the order of 1 per cent. Details will be reported elsewhere.

Effect of Mechanical Tension on Electrical Resistance.—For Li, Ca and Sb, as in the case of most metals, the resistance increases with the tension, whereas for Bi and Sr the coefficient is negative. Details will be reported elsewhere.

Modified Electron Theory of Electrical Conductivity has already been suggested by the author. It is assumed that the number of free electrons is relatively small; that their mean free path is many times the atomic diameter and depends on the amplitude of atomic vibration; and that the natural velocity of the electrons has the equipartition value. It is here *discussed in the light of the above new experimental data.* The deviations from Ohm's law support the theory since they require long mean free paths. For normal atoms for which the resistance decreases with increasing pressure, the electrons must pass directly from atom to atom through intervening atoms; but for the abnormal atoms Li, Ca and Sb, with both pressure and tension coefficients positive, the electrons seem to pass in channels between the atoms, somewhat as in Wien's theory. Diagrams are given showing the relation of the channels to the crystal structure. This simple conception enables the various coefficients of resistance to be connected quantitatively. The tension and temperature coefficients are calculated in terms of the pressure coefficients and the elastic constants and are found to agree approximately with the observed values.

Pressure Coefficient of the Wiedemann-Franz Ratio has been found to be negative for nine out of the eleven metals tested; that is, the thermal conductivity increases with pressure less rapidly than the electrical conductivity. Details will be reported elsewhere.

Elastic Wave Theory of the Atomic Part of Thermal Conduction in Metals.—The above result for the pressure coefficient means that an important part, probably at least one third, of the thermal conduction in these metals is performed by atoms, a conclusion confirmed by a comparison of Lorentz's theoretical value of the Wiedemann-Franz ratio with the experimental value. As a crude *picture of the atomic conduction*, it is suggested that the atoms are arranged in coherent strings separated from each other by gaps which each shift in position by the diameter of an atom each time the string on either side is hit, just like gaps between strings of billiard balls. Thermal energy is transferred when the gap shifts. By calculation, the maximum rate of propagation of a gap comes out about half the speed of sound in the metal, much less than the electronic velocity. The theory of electrical conduction already presented suggests that the length of the coherent strings of atoms is the same as the free path of the electrons, thus making possible a connection between the electronic and atomic contributions to thermal conductivity. If the number of atoms is of the order of 20 times the number of free electrons, as is to be expected from the above theory of electrical conductivity, then atomic conductivity comes out of the proper order of magnitude. A discussion of the temperature and

pressure coefficients of the atomic conductivity adds further evidence in favor of the probability of this theory. *Comparison with other theories.* It is similar to Debye's concept of thermal conduction in a crystal, but differs from Hall's ionization theory which, it is concluded, probably can account for only a small part of the conduction.

Introduction.

In two papers in preceding numbers of this journal [1, 2] I have presented certain theoretical considerations with regard to the electron mechanism of electrical and thermal conduction in metals. Since writing these two papers, I have obtained three new sorts of experimental evidence bearing on the electron theory. In the first place, I have succeeded in detecting and measuring a departure from Ohm's law at high current densities in metallic gold and silver. In the second place, I have measured the effect of pressures to 12,000 kg./cm.^{2} on the thermal conductivity of eleven metals. And thirdly, I have measured the effect of mechanical tension on the resistance of those metals which are abnormal in that their resistance increases under hydrostatic pressure. It is the purpose of this paper to discuss the bearing of these new data on the electron theory of conduction as I have previously given it.

The theory which I have presented is a free path theory. It differs from the classical theory, which is also a free path theory, in the following respects: the number of free electrons is supposed small compared with the number of atoms, so that the free path is long compared with the distance between atomic centers, and the variations of resistance under changes of temperature or pressure are computed in terms of the variation of free path, which may be found from the variation of amplitude of atomic vibration, and in terms of the natural velocity of the electrons, for which the equipartition value is assumed, as in the classical theory. The evidence for the equipartition velocity is twofold: it is required to account for the universal value of the Wiedemann-Franz ratio, and it is also required to account for the universal value of the temperature coefficient of resistance.

The evidence seemed to be that there are two essentially different types of mechanism by which electrons pass through a metal. By far the most usual type is that of those metals whose resistance decreases with increasing pressure. In these metals it is probable that the electrons pass directly from atom to atom through the substance of the atom itself. There are a few metals, however, whose resistance increases under pressure. There are two possibilities in the way of mechanism for these abnormal metals. In the first place, the mechanism may be like that

[1] P. W. Bridgman, Phys. Rev., 9, 269–289, 1917.

[2] P. W. Bridgman, Phys. Rev., 17, 163–194, 1921.

above in that the electrons pass from atom to atom through the substance of the atom, but the law of force between atoms may be abnormal so that there are abnormalities in the way in which the amplitude changes with pressure (bismuth type), or the electrons may pass between the atoms in natural channels, much after the manner of the theory of Wien [3] (lithium type).

The Evidence from Ohm's Law.—The data are to be presented in detail in another place. The experimental fact is that the resistance of gold and silver in the shape of thin leaf has been found to increase by something of the order of one or two per cent. at current densities of the order of $5 \times 10^{\circ}$ amp./cm^2. Now J. J. Thomson [4] showed long ago on the basis of the classical theory that the resistance would be expected to increase at very high current densities, because the velocity of drift imparted to the electrons by the external field would no longer be small compared with the natural velocity of the electrons. It is evident that the velocity of drift imparted by the external field will be greater the longer the free path, that is, the longer the time in which the field has a chance to act on the electron without interference. On the basis of the length of free path assumed by the classical theory, which is equal to or less than the distance between atomic centers, the departures from Ohm's law would not begin to play an important rôle at currents below 10^{11} amp./cm^2. Since I am also assuming a free path mechanism, the fact that I find departures from Ohm's law at densities so much lower than predicted by the classical theory must mean that the free paths are much longer than the distance between atomic centers. Now this is exactly the kind of free path that other kinds of evidence have already made seem probable to me, so that this new experimental fact affords confirmation of the theory.

It is unfortunate that I can see no way of calculating exactly what the free path is in terms of the departures from Ohm's law. Such a computation involves a knowledge of the small departures from Maxwell's distribution law for the electrons at high fields, and this again I believe involves a detailed knowledge of the whole atomic structure. I am compelled therefore at present to leave this new experimental evidence with the bare statement that it makes exceedingly probable a long free path, and is in so far in accord with my theory.

Effect of Pressure on Thermal Conductivity.—The data for eleven metals are to be published in another place, to which reference must be made for the details. Only normal metals, whose electrical resistance decreases

[3] W. Wien, Columbia Lectures, 1913, 29–48.

[4] J. J. Thomson, The Corpuscular Theory of Matter, 1907, p. 55.

under pressure, were measured. The broad facts are that the thermal conductivity may either increase or decrease under pressure. For only two metals was the increase of thermal conductivity greater than the increase of electrical conductivity; for these two metals (lead and tin) the Wiedemann-Franz ratio increases under pressure, for the other metals it decreases.

In my theory I took over without essential modification the classical picture of thermal conduction as performed by the same electrons that carry the current. The reason for this was that I could see no other way of accounting for the approximate constancy of the Wiedemann-Franz ratio for different metals, and this seemed to me the one most striking and outstanding fact with regard to thermal conduction. So far as the conduction of electrical current and heat is by the same mechanism, one may expect the effect of pressure on the electrical and thermal conductivity to be the same, and hence the pressure coefficient of the Wiedemann-Franz ratio to be zero. The new experimental evidence requires therefore a reconstruction of our previous picture of the mechanism of thermal conduction. The modification is not very serious, however, and does not require us to abandon anything of our previous position. It has of course always been known that the picture of thermal conduction offered by the classical theory is not complete in that it neglects the part of the heat carried by the atoms. We now have to inquire what the probable magnitude of this neglected part of the thermal conductivity is, and whether it is not capable of explaining the new facts.

With regard to the probable magnitude of the atomic part of thermal conduction, it is well known that the original value of the Wiedemann-Franz ratio deduced by Drude from elementary considerations agrees with the experimental facts much better than the more rigorous value deduced by Lorentz,[5] Bohr,[6] and others. Lorentz's value is only two thirds that of Drude, and Drude's is slightly less than the experimental value. If we accept Lorentz's value as the one properly to be deduced from the theory, and his work has been abundantly checked by others, this would mean that the atomic part of the electrical conductivity may be at least half as large as the electronic part. This is a fairly large part to have at our disposal.

Now the electronic part of the thermal conductivity must increase under pressure at the same rate as the electrical conductivity. But the atomic part may conceivably either increase or decrease, and so the pressure coefficient may be either positive or negative. The only absolute requirement here is that the total decrease of conductivity under

[5] H. A. Lorentz, The Theory of Electrons, p. 65.

[6] N. Bohr, Studier over metallernes Elektrontheori, Copenhagen, 1911.

pressure must never be so great as to more than use up the initial atomic contribution, because the atomic contribution must always remain positive. In the experimental paper this question is examined in detail, and I have shown that there is never any trouble on this score.

We now have to consider more in detail what the nature of the atomic part (more specifically, the part not determined by the classical electron free path mechanism) of the thermal conductivity may be, and what may be expected as to the sign of its pressure coefficient. The following picture seems to satisfy the requirements as far as order of magnitude goes, and has the advantage of using part of the same mechanism that we have invoked to explain electrical conductivity. In the normal metal I have thought of the electron as passing through the substance of the atom, with a free path a good many atomic diameters long. A crude picture of this state of affairs is that the atoms in a metal are separated into many coherent strings, one string separated from the next by a distance greater than the normal, that is, by a "gap." These strings are in a constant state of flux, as the position of the gaps is continually changing. The length of the string is the free path of the electrons for electrical conduction. The mechanism by which the gap wanders about in the metal is an elastic mechanism; we imagine the head of the string being struck by the rear atom of the string ahead of it; the impacting atom sticks to the string, an impulse travels along the string, and the rear atom flies off, exactly as when a row of billiard balls in contact is struck by a single ball head on. Under the most favorable conditions the gap cannot travel ahead by more than the diameter of an atom during the natural period of atomic vibration. Now the natural period is known for a number of metals, and a numerical calculation shows that for all metals this maximum velocity of propagation of the gap is about one half the velocity of sound. This is much less than the velocity of free flight of the electrons. At 0° C. this latter is about 1.7×10^7 cm./sec., and the maximum velocity of sound for any metal is about 5×10^5. This means that for the electrons the gaps are practically stationary, so that our former picture of conduction is not at all affected by the motion of the gaps.

Now the mechanism of translation of the gaps, that is, the sticking of an atom to the head of the string and the flying off of one from the rear, is evidently one that is capable of conducting heat, if there is a temperature gradient in the metal. Precisely the same analysis may be applied to this case as to the ordinary kinetic problem of heat transfer. The important feature is that the free path for heat transfer is the same as the free path for electrical conduction. In my theory of conduction I

have assumed that there is equipartition of energy between the atoms and electrons. Let us call $f(\theta)$ the energy of either atom or electron as a function of temperature. Then for the part of the thermal conductivity due to the atoms, the ordinary transport analysis will give the formula

$$\mu_a = nl\frac{df}{d\theta},$$

and for the part due to the electrons the same analysis will give

$$\mu_e = \frac{1}{3}N_e v_e l\frac{df}{d\theta}.$$

Here N_e is the total number of free electrons (that is, electrons which take part in the conduction process) per cm.^{3}, v_e is the velocity of the electrons, l is the free path, and n is the number of atomic transfers of energy per second across unit section. Of these quantities n is the only one requiring further discussion. Its exact value will depend to a high degree on the structure of the crystal and the perfection of the fit between neighboring atoms, but we can at least set an upper limit. The maximum number of transfers of energy down each string of atoms is evidently the frequency of atomic vibration, ν, for this is the maximum number of collisions of the head of the string with the rear of the next. The number of strings crossing unit section is the number of atoms in unit section, or $N_a^{2/3}$, where N_a is the number of atoms per cm^3. Hence an upper limit for n is $\nu N_a^{2/3}$. If now we substitute this upper limit for n in the formula for μ_a, and take the ratio of the atomic to the electronic conductivity, we get

$$\frac{\mu_a}{\mu_e} = \frac{N_a}{N_e}\left(\frac{3\nu}{v_e N_a^{1/3}}\right).$$

The reasonableness of this may be checked as far as order of magnitude goes as follows. In the first place, μ_a/μ_e must be in the neighborhood of 0.5, for the actual Wiedemann-Franz ratio is usually about 50 per cent. greater than Lorentz's theoretical value. In the second place, my theory of electrical conduction demands that N_a/N_e be large, perhaps of the order of 100 or 1,000. If the velocity of migration of the gaps through the metal is the maximum, then N_a/N_e given by the above formula must also be of the same order, but since the migration velocity may well be much below the maximum, we may expect N_a/N_e to be smaller than the above, but still materially larger than unity. I have made the calculation in this way, putting $\mu_a/\mu_e = 0.5$, for the metals Al, Cu, Zn, Ag, and Pb. Nernst [7] gives the value of the frequency of these, and the other

[7] W. Nernst, Wolfskehlstiftung Vorträge, Göttingen, 1914, p. 77.

constants are well known. I find the following values respectively for N_a/N_e; 10, 15, 15, 15, 30. The order of magnitude of these is hence about what would be expected.

Another check as to the probability of this point of view is afforded by the variation of thermal conductivity with temperature. My theory of electrical conductivity gives a variation of electrical resistance as the absolute temperature, which of course agrees very approximately with the facts. Now theoretically the Wiedemann-Franz ratio is proportional to the absolute temperature; this means that that part of the thermal conductivity due to the electrons is independent of the temperature. This enables us to find at once the temperature coefficient of the atomic part of the thermal conduction. To find this, differentiate μ_e logarithmically, obtaining

$$\frac{1}{\mu_e}\frac{d\mu_e}{d\theta} = \frac{1}{N_e}\frac{dN_e}{d\theta} + \frac{1}{v_e}\frac{dv_e}{d\theta} + \frac{d}{d\theta}\log\left(l\frac{df}{d\theta}\right).$$

We suppose, as always, that N_e is constant, and since $d\mu_e/d\theta$ is to be zero, this gives

$$\frac{d}{d\theta}\log\left(l\frac{df}{d\theta}\right) = -\frac{1}{v_e}\frac{dv_e}{d\theta} = -\frac{1}{2\theta},$$

since v_e^2 is proportional to θ. Now differentiate μ_a logarithmically, obtaining

$$\frac{1}{\mu_a}\frac{d\mu_a}{d\theta} = \frac{1}{n}\frac{dn}{d\theta} + \frac{d}{d\theta}\log\left(l\frac{df}{d\theta}\right)$$
$$= \frac{1}{n}\frac{dn}{d\theta} - \frac{1}{2\theta}.$$

Now assuming that n is a fixed fraction of its maximum value, the variation of n with temperature is small, since that of its factors N_a and ν is small, and may be neglected. (I have previously discussed the variation of ν with temperature.) [8] Hence finally,

$$\frac{1}{\mu_a}\frac{d\mu_a}{d\theta} = -\frac{1}{2\theta}.$$

If now we attempt to allow for a change with temperature of the fractional part of its maximum value which n assumes, the probability seems to me that this fractional part will increase with rising temperature, since the change in amplitude of atomic vibration with rising temperature is large compared with the change in the distance of separation of atomic centers. This would mean that the temperature coefficient of the atomic part of thermal conductivity is more nearly positive than $-1/2\theta$.

[8] Reference 1, equation (4), p. 271.

We have now found that the atomic part of the thermal conductivity decreases with rising temperature. The other part remains constant, and hence we would expect the temperature coefficient of thermal conductivity of all metals to be negative, and to be largest numerically in those metals in which the atomic share in conductivity is largest. Now a large Wiedemann-Franz ratio means a larger proportional atomic conductivity. Hence if we plot Wiedemann-Franz ratio against temperature coefficient of thermal conductivity, we would expect the high values of the one to go with the high values of the other. I have plotted these values in Fig. 1 for most of the metals of this paper. It is known

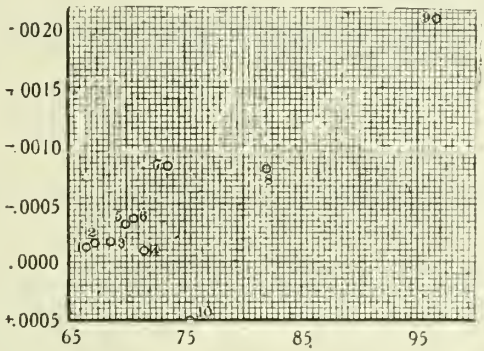


Fig. 1.

Temperature coefficient of thermal conductivity (ordinates) against Wiedemann-Franz ratio times 10^{-9} (abscissae). The metals shown are as follows: 1 Cu, 2 Zn, 3 Ag, 4 Pb, 5 Ni, 6 Cd, 7 Sn, 8 Fe, 9 Bi, 10 Pt.

that the temperature coefficient is extremely subject to experimental error, and different observers do not always agree. I have used the data of Jaeger and Diesselhorst,[9] by far the best, who made all the different sorts of measurements on the same samples of metal. Only for nickel do Jaeger and Diesselhorst not give the coefficient, and I have taken the temperature coefficient of conductivity from another observer.[10] All the metals of my pressure study are here included except antimony. With the exception of platinum, whose temperature coefficient of thermal conductivity is + 0.0005, and hence is entirely out of the class of the other metals, the correlation is strong between Wiedemann-Franz ratio and temperature coefficient, and hence lends probability to our view. With regard to platinum it may be said that its electrical resistance also behaves abnormally with regard to temperature, since it is one of a very few metals for which the curve of resistance against temperature is concave toward the temperature axis.

[9] W. Jaeger und H. Diesselhorst, Phys. Tech. Reichsanstalt, Wiss. Abh. 3, 269–425, 1900.
[10] M. F. Angell, Phys. Rev., 33, 421–432, 1911.

This point of view imposes a limit on the possible temperature coefficient of thermal conductivity. This must not be so high that the coefficient of the atomic part alone gets numerically greater than $-1/2\theta$, or about -0.0018. This is true for all the metals above except bismuth, which of course is abnormal in other respects. The restriction is most exacting in the case of tin, but is still met with a few per cent. margin of safety.

So much for the inherent probability of our picture of the part of thermal conductivity done by the atoms. Now with regard to the effect of pressure on this part of the conductivity, we may recognize two opposing tendencies.

Differentiate μ_a and μ_e logarithmically at constant temperature, obtaining

$$\frac{1}{\mu_a}\left(\frac{\partial \mu_a}{\partial p}\right)_\theta = \frac{1}{n}\left(\frac{\partial n}{\partial p}\right)_\theta + \frac{\partial}{\partial p_\theta}\log\left(l\frac{df}{d\theta}\right)$$

and

$$\frac{1}{\mu_e}\left(\frac{\partial \mu_e}{\partial p}\right)_\theta = \frac{1}{N_e}\left(\frac{\partial N_e}{\partial p}\right)_\theta + \frac{1}{v_e}\left(\frac{\partial v_e}{\partial p}\right)_\theta + \frac{\partial}{\partial p_\theta}\log\left(l\frac{dt}{d\theta}\right).$$

We suppose that N_e remains constant, and our assumption with regard to equipartition also means that v_e is constant at constant temperature. Hence $(1/\mu_a)\ (\partial\mu_a/\partial p)_\theta$ differs from $(1/\mu_e)\ (\partial\mu_e/\partial p)_\theta$ only by the term $(1/n)\ (\partial n/\partial p)_\theta$. Now in general we may put $n = \beta\nu N_a^{2/3}$, where β is a factor which at the maximum can reach only unity. The variations of N_a with pressure are comparatively unimportant, so that if β does not change, the proportional change of n is determined by the proportional change of ν. This has been computed in a previous paper.[11] It is the negative of the proportional change of amplitude, which in turn is approximately one half the pressure coefficient of resistance. ν therefore increases under pressure, and at such a rate as to contribute to the atomic part of the conductivity an increase about one half as rapid as the increase of electrical conductivity. The other factor, β, however, is the one that is likely to be important. Our previous discussion of the order of magnitude of N_a/N_e shows that β is probably much below its maximum value of 1, so that there is plenty of room for variations in either direction. I do not believe that we can predict its precise manner of variation until we know a great deal about atomic structure and the arrangement of the atoms in the crystal. The factor β is a measure of the frequency with which energy is handed on from one string of atoms to the next, and it is also a measure of the speed of migration of the gaps through the metal. Now a gap is a joint or fissure in the atomic structure due to

[11] Reference 1, equation (5), p. 271.

temperature agitation. Its permanence, or its ease of migration, will obviously depend on the details of the structure. It seems quite plausible to me that the speed of migration or mobility might either increase or decrease under pressure, with the probability that in most cases it will decrease, because with increasing pressure a group of atoms must find it more difficult to escape from their lack of fit by handing it on to the neighbors. An escape from lack of fit would seem to involve a local and temporary increase of volume, which is against the urge of the external pressure. The mobility of the gaps may involve something analogous to the internal viscosity of the metal. This has never been measured under pressure, but it is known that the viscosity of liquids increases greatly with pressure, and that the increase is proportionally greater for those substances with a high absolute value of viscosity, so that it is not unreasonable to expect a comparatively large pressure effect on the internal viscosity of metals.

As a matter of fact, it does turn out in the majority of cases that the increase of thermal conductivity is smaller than the electrical conductivity, or else is negative, so that the atomic part of thermal conductivity in many cases must decrease. In the case of lead and tin only is the increase of thermal conductivity so large as to indicate that for them β may increase with pressure.

This picture of the atomic part of thermal conduction is in many respects like Debye's[12] concept of thermal conduction in a crystal. He has heat conducted by elastic waves, which are dissipated by the lack of perfect homogeneity of the material. The waves have an equivalent "free path" defined in terms of the distance between inhomogeneities. He finds the cause of the inhomogeneities in local chance variations from the mean density, which he calculates by the thermodynamic formulas for "Schwankungen." His local inhomogeneities evidently function as my gaps, and in fact may be the same thing physically. Debye did not discuss metallic conduction. My assumption that the free path of the elastic waves is the same as that of the electrons seems a most natural one, but so far as I know, has not been employed before. Notice in this connection that the purely atomic part of the conductivity in a metal is large compared with the total conductivity of such crystals as rock salt.

There are other possible factors to be taken into account. In the first place, the free path is not actually so cleanly defined a thing as we have supposed above. As the electrons pass from atom to atom they are subject to a certain amount of interference at every passage; there

[12] P. Debye, Wolfskehlstiftung Vorträge, Göttingen, 1914, 43–60.

is no catastrophic change every now and then as we have supposed, and the free path idea can only be a rough description of an average state of affairs. The same sort of thing must of course be recognized in applying kinetic theory to condensed gases or liquids. Kleeman has emphasized in his recent book[13] this indefinite character of the concept of a free path, and has shown that a great many kinds of free path must be recognized. For any particular sort of phenomenon, mean free path is defined in a corresponding particular way. The free path for viscosity, for example, is defined in terms of velocity transfer, and for heat conduction in terms of energy transfer. Kleeman has shown that different sorts of free path may differ in rare cases by factors of as much as 10. We would expect to find the same sort of thing in a metal, so that the free path of electrical conductivity (which is concerned with a velocity transfer) would not be the same as the free path of thermal conductivity (which is concerned with a kinetic energy transfer). This may account partly for the difference between the observed and computed Wiedemann-Franz ratio. It is also possibly conceivable that the two different kinds of path should be differently affected by pressure, so that the pressure coefficients might have opposite signs. The theory is not far enough advanced, however, to allow us to make any quantitative use of it. All that has hitherto been done is to calculate back from the experimental data to show that there must be different kinds of path if the kinetic formulas are correct. We cannot yet solve the direct problem of predicting in terms of the atomic structure what the relation between the different sorts of path will be, and it is the direct problem that must be solved for the present purpose.

There is a second possibility that I have considered. Professor Hall[14] has a theory of thermal conduction in terms of the heat of ionization of the atoms. This sort of a mechanism seems at first sight exactly what we need to explain the pressure coefficient of thermal conduction, because it is natural to suppose that the heat of ionization becomes less as the pressure becomes greater, and for this reason the thermal conductivity would decrease with rising pressure. But there is another factor to consider, namely, the number of ions per cm^3. If this number is connected with the heat of dissociation by the ordinary formula $n = n_0 e^{-(w/K\theta)}$, a decrease in the heat of ionization will be accompanied by an increase in the number of ions, so that for this reason the thermal conductivity will increase. A numerical discussion with probable values, for instance assuming such a heat of ionization that the atoms are 1/1,000 ionized, shows that the increase of numbers far overbalances the decrease of

[13] R. D. Kleeman, A Kinetic Theory of Gases and Liquids, Wiley and Sons, 1920.

[14] E. H. Hall, PHYS. REV., 11, 329, 1918.

heat of ionization, so that on the whole the conductivity will increase under pressure, instead of decrease. Another objection to Professor Hall's theory is that it gives no account of the Wiedemann-Franz ratio. Of course a mechanism like that of Professor Hall's theory must be present in the metal, simply because the presence of free electrons involves the presence of ions, but my own feeling is that this part of thermal conduction is not so important as some others.

Effect of Tension on the Resistance of the Abnormal Metals.—The experimental results are published at length in another place. Briefly, the essential facts are these. There are five metals known to be abnormal in that their resistance increases under pressure, Bi, Sb, Li, Ca, and Sr. Of these only two, Bi and Sr, are abnormal also with respect to the effect of tension, in that their resistance decreases under tension. The resistance of Li, Ca, and Sb increases under tension, as is normal. In the detailed paper I have shown that the metals with a "Bismuth mechanism" would be expected to act as Bi does under both tension and pressure, and that metals of the "Lithium mechanism" would be expected to act like Sb, Li, and Ca under tension and pressure. Considerations were given that made it likely that both sorts of mechanism were involved in Sr.

It is my purpose here to consider further the three metals Li, Ca, and Sb. The account which I have previously given of the effect of pressure and temperature does not apply to metals of this type. Further, the three metals are of particular interest in the apparently great simplicity of their mechanisms. This simplicity makes possible a deduction of expressions for the temperature and tension coefficients of resistance in terms of the pressure coefficient and other unrelated data.

In metals of the lithium type, the electrons are to be thought of as travelling in channels between the atoms. Under external changes, the channels change in dimensions, both because the centers of the atoms are changed in position and because the amplitude of atomic vibration is changed. For those changes which take place at constant temperature our problem is to deduce the changes of resistance in terms only of the changes in cross section of the channels; if the temperature changes also, the change of resistance involves both the change of dimensions of the channels and the changes of velocity of the electrons with temperature.

The details of the computation will involve a knowledge of the crystalline structure and the relation of the channels to that structure. The structure of lithium is known to be space centered cubic;[15] the structure of

[15] A. W. Hull, Phys. Rev., 10, 689, 1917.

calcium is face centered cubic;[16] the structure of antimony is complicated,[17] consisting of two interpenetrating lattices, but it is very approximately simple cubic in structure, and for our purposes it will be good enough to treat it as simple cubic.

In Fig. 2 is shown a view of spheres piled in space centered cubic

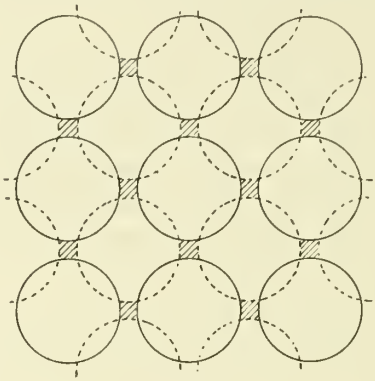


Fig. 2.

One view of spheres in contact in space centered cubic arrangement. The shaded areas indicate open channels.

arrangement, the diameters of the spheres being such that they are in contact with each other. The dotted circles show the spheres in the layer below the full spheres. The diagram shows that there are open channels between the spheres through which the electrons may pass. Of course if the atoms are not large enough to be in mutual contact, the channels are even larger.

In Fig. 3 is shown one view of spheres in mutual contact in face centered

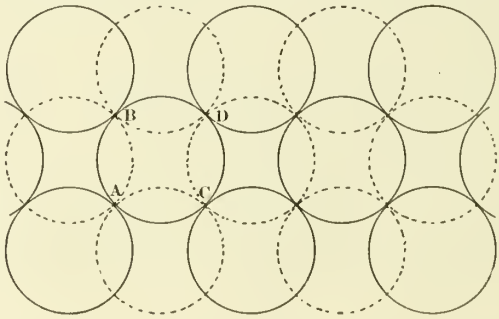


Fig. 3.

One view of spheres in contact in face centered cubic arrangement. Channels open where shown by the letters if the distance between atomic centers is slightly increased.

[16] A. W. Hull, PHYS. REV., 17, 42–44, 1921.

[17] R. W. James and N. Tunstall, Phil. Mag., 40, 233–239, 1920.

cubic arrangement. Now in this structure there are no open straight channels, but if the centers of the spheres are held fast, while their radii decrease, channels open in the locations indicated by the letters, and the plane section of the crystal becomes similar to that of the space centered crystal of Fig. 2. In fact Fig. 3 goes into Fig. 2 on rotation through 45°. (The distance of separation of the planes of the full and the dotted spheres does not become the same for the two kinds of crystal, however.) Now the crystallographic evidence proves that in the crystal of metallic calcium the atoms cannot be in contact,[18] and hence we assume the channels in metallic calcium to be in the place shown.

If the structure is simple cubic with the spheres in contact, the spaces between the full circles of Fig. 2 show the location of the channels. It seems more likely, however, that the atoms of Sb are not spherical, but are more nearly cubic, filling the space more completely. One reason why this seems probable is that spheres in simple cubic piling are exceedingly unstable, whereas cubes in simple cubic piling are as stable as possible. Fig. 4 therefore probably represents a closer approach to the

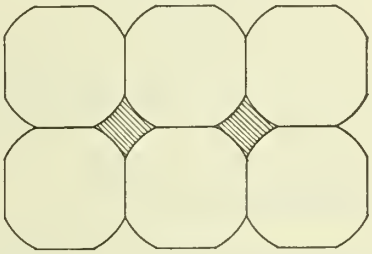


Fig. 4.

One view of approximately cubic atoms in simple cubic piling. The shaded regions show open channels.

case for antimony, the atoms having the shape of rounded cubes, and the channels being in the grooves between the edges, as shown.

We have now to consider the effect of temperature agitation on the size of the channels. The atom is to be thought of as of a fixed size, but at higher temperatures it occupies an effectively larger space in virtue of its temperature agitation. Under these conditions the section of the channel for all three types of crystal structure may be represented approximately as in Fig. 5. The full circles show the outlines of the stationary atoms, and the dotted circles the space effectively occupied by them in virtue of temperature agitation. If we call "a" the radius of the atom, α its amplitude of temperature vibration, c the width of the

[18] Reference 16, p. 44.

channel at the place shown, and L the distance between atomic centers in the direction indicated, then

$$L = 2a + 2\alpha + c.$$

Call δ the closest distance of approach of atomic centers. There is a relation between L and δ which is different for the different crystal systems.

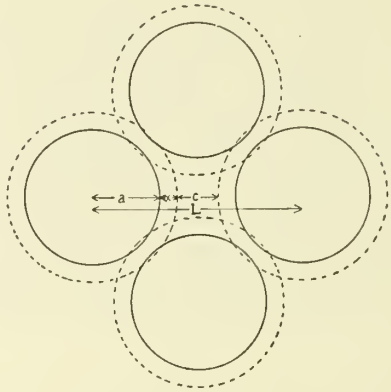


Fig. 5.

Shows the effective relations between the size of the atom, the space occupied by temperature agitation, and the open channels.

Simple cubic, $L = \sqrt{2}\delta$,
Face centered cubic, $L = \delta$,

Space centered cubic, $L = \frac{2}{\sqrt{3}}\delta$.

We now assume the free path of the electron, l, to be proportional to the section of the channel, which to a sufficient degree of approximation we may put equal to c^2. (The precise factor of proportionality between the area of the channel and c^2 does not enter the result so long only as it stays constant.) The resistance is inversely as l, and directly as v, the electronic velocity.

Our program calls in the first place for a computation of c in terms of the pressure coefficient of resistance, and then for a computation of the tension and temperature coefficients.

Denote the resistance by w. Then at constant temperature,

$$w = \frac{\text{const.}}{c^2},$$

and

$$\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_\theta = -\frac{2}{c}\left(\frac{\partial c}{\partial p}\right)_\theta,$$

whence

$$c = -\frac{2\left(\frac{\partial c}{\partial p}\right)_{\theta}}{\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_{\theta}}.$$

$(1/w)\ (\partial w/\partial p)_\theta$ is known experimentally. To find $(\partial c/\partial p)_\theta$ we have

$$\left(\frac{\partial L}{\partial p}\right)_{\theta} = 2\left(\frac{\partial \alpha}{\partial p}\right)_{\theta} + \left(\frac{\partial c}{\partial p}\right)_{\theta}.$$

$(\partial L/\partial p)_\theta$ may be found as follows. Obviously

$$\frac{1}{L}\left(\frac{\partial L}{\partial p}\right)_{\theta} = \frac{1}{3}\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_{\theta},$$

and the cubic compressibility is known. We now need the absolute value of L. The absolute value of δ may be found in terms of the atomic volume, V, and the mass of the hydrogen atom by the formula

$$\delta = \gamma(m_H V)^{1/3},$$

where γ is a factor depending on the crystal system.

Simple cubic, $\gamma = 1$,

Face centered cubic, $\gamma = (2)^{1/6} = 1.123$,

Space centered cubic, $\gamma = \frac{\sqrt{3}}{2^{2/3}} = 1.09$.

Using the above equations for L in terms of δ, we can now find the absolute value of L, and hence can compute $(\partial L/\partial p)_\theta$.

Our next problem is to compute $(\partial \alpha/\partial p)_\theta$. In a previous paper[19] I have shown that

$$\frac{1}{\alpha}\left(\frac{\partial \alpha}{\partial p}\right)_{\theta} = -\left(\frac{\partial v}{\partial \theta}\right)_{p} \Big/ C_p.$$

Hence we can find $(\partial \alpha/\partial p)_\theta$ if we can find α. To get α, we use the equipartition law. In a solid, the atom has six degrees of freedom, and therefore its maximum kinetic energy is twice the energy of a gas molecule at the same temperature. If the atom executes simple harmonic vibrations of frequency ν, at 300° Abs. we have

$$\frac{m}{2}4\pi^2\nu^2\alpha^2 = 2 \times 300 \times 2 \times 10^{-16}.$$

The problem of determining α is reduced to determining ν. The best way would be from the specific heats at low temperatures, but the data

[19] Reference 1, equation (6), p. 271.

do not seem to have been obtained. In default of a better, we may use Lindemann's formula in terms of melting temperature, atomic weight, and atomic volume

$$\nu = 3.08 \times 10^{-12} \sqrt{\frac{T_s}{m V^{2/3}}}.$$

We now have all the material to compute the required quantities, eventually getting c, and also a, the atomic radius.

Our next task is to compute the changes of resistance under tension. Our general picture is as follows. When the metal is stretched longitudinally it contracts transversely, the channels becoming constricted, and the resistance increases. Since the tension is applied at constant temperature, we have as before $w = \text{const.}/c^2$, and

$$\frac{1}{w}\left(\frac{\partial w}{\partial T}\right)_\theta = -\frac{2}{c}\left(\frac{\partial c}{\partial T}\right)_\theta,$$

where T denotes tension. $(\partial c/\partial T)_\theta$ can be found from the equation $L = 2a + 2\alpha + c$, provided we can get $(\partial \alpha/\partial T)_\theta$, for $(\partial L/\partial T)_\theta$ may be obtained in terms of the elastic constants. In fact

$$\frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_\theta = -\frac{\sigma}{E},$$

where σ is Poisson's ratio, and E is Young's modulus. With regard to the changes of α under tension, we do not know much. In the first place, the substance becomes anisotropic under tension, so that changes of α are different in different directions. It is probable, however, that the changes of α are not important, and we shall neglect them. This may be approximately justified as follows. Neglecting anisotropy, a thermodynamic discussion of the changes of the average α with tension may be carried through on the same basis as the preceding discussion for the changes of α with pressure.[20] In that analysis we should have to replace p by T, and v (volume) by l (length). We would find for the final result

$$\frac{1}{\alpha}\left(\frac{\partial \alpha}{\partial T}\right)_\theta = -\left(\frac{\partial l}{\partial \theta}\right)_T \Big/ C_T.$$

Now C_T, specific heat at constant tension, is very nearly the same as C_p, and $(\partial l/\partial \theta)_T = \frac{1}{3}(\partial v/\partial \theta)_p$. Therefore the proportional change of α under 1 kg./cm.^{2} tension is approximately one third of its change under 1 kg./cm.^{2} pressure. But on the other hand, the changes of dimensions under 1 kg. tension are considerably larger than under 1 kg. pressure, so that

[20] Reference 1, p. 271.

it is probable that under tension changes of α are relatively much less important than under pressure. But an examination of the figures above will show that even under pressure the changes of α are not important compared with the changes of dimensions (L), and we shall therefore neglect $(\partial\alpha/\partial T)_\theta$.

Hence we have

$$\left(\frac{\partial c}{\partial T}\right)_\theta = \left(\frac{\partial L}{\partial T}\right)_\theta = -\frac{L\sigma}{E},$$

and

$$\frac{1}{w}\left(\frac{\partial w}{\partial T}\right)_\theta = \frac{2}{c}\frac{L\sigma}{E}.$$

The tension coefficient is computed in this way and listed in the table. The computed value is 2/3 the observed value for Li, and 3/2 of it for Ca and Sb.

Finally we have to compute the temperature coefficient of resistance. According to our previous theory the changes of resistance with temperature depend on two factors; one of these is the change of the velocity of the electrons with temperature. This part of the change is $1/2\theta$, and is the same now as previously. The second part of the change of resistance is due to the change of free path. For normal metals I have shown that this change is also $1/2\theta$. The free path mechanism of these three abnormal metals is, however, entirely different from that of the normal metals, and the previous analysis fails. Our problem is to recompute the second part of the variation.

Now for changes of temperature, the conditions are the exact reverse for changes of tension. Here the changes of dimensions of the metal are unimportant compared with the changes of amplitude of atomic vibration. One may easily check this by a simple calculation. (I have already gone into the matter in connection with the pressure effects.) [21] In order to entirely get rid of the effect of changing dimensions, we will compute the temperature coefficient of resistance at constant volume instead of at constant pressure. The two coefficients differ by only a few per cent.; the exact formulas will be found in the place last cited.

For changes of resistance at constant volume we now have

$$\frac{1}{w}\left(\frac{\partial w}{\partial \theta}\right)_v = \frac{1}{2\theta} - \frac{2}{c}\left(\frac{\partial c}{\partial \theta}\right)_v.$$

To find $(\partial c/\partial\theta)_v$, we differentiate the equation $L = 2a + 2\alpha + c$, obtaining

$$\left(\frac{\partial c}{\partial \theta}\right)_v = -2\left(\frac{\partial \alpha}{\partial \theta}\right)_v.$$

[21] Reference 1, p. 272.

Metal.	$\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_\theta$.	$\frac{1}{\alpha}\left(\frac{\partial \alpha}{\partial p}\right)_\theta$.	ν.	δ.	L.	$\left(\frac{\partial L}{\partial p}\right)_\theta$.	α.	$\left(\frac{\partial \alpha}{\partial p}\right)_\theta$.
Li.....	6.8×10^{-6}	-10×10^{-6}	10.6×10^{12}	3.11×10^{-8}	3.60×10^{-8}	-10.8×10^{-14}	2.16×10^{-9}	-21.6×10^{-15}
Ca.....	10.6	-7.7	5.4	3.94	3.94	-7.5	1.77	-13.7
Sb.....	12.2	-2.26	3.23	3.18	4.46	-3.57	1.71	-3.86

	$\left(\frac{\partial c}{\partial p}\right)_\theta$.	c.	a.	$-\frac{2}{c}\left(\frac{\partial c}{\partial T}\right)_\theta$.	$\frac{1}{w}\left(\frac{\partial w}{\partial T}\right)_\theta$.	$\frac{1}{\theta}\left(\frac{1}{2}+\frac{2\alpha}{c}\right)$	$\frac{1}{w}\left(\frac{\partial w}{\partial \theta}\right)_v$.
Li.....	-6.5×10^{-14}	1.91×10^{-8}	0.62×10^{-8}	3.2×10^{-5}	4.8×10^{-5}	.0027	.0043
Ca.....	-4.8	0.905	1.34	1.24	0.84	.0033	.0030
Sb.....	-2.80	0.459	1.83	0.73	0.50	.0046	.0049

But we have already found that

$$\frac{1}{\alpha}\left(\frac{\partial\alpha}{\partial\theta}\right)_v = \frac{1}{2\theta}.$$

Hence finally

$$\frac{1}{w}\left(\frac{\partial w}{\partial\theta}\right)_v = \frac{1}{\theta}\left(\frac{1}{2} + 2\frac{\alpha}{c}\right).$$

The results of computation by this formula are given in the table. The result is distinctly low for Li, but is as close to the experimental value as could be desired for Ca and Sb. The agreement would be expected to be closer for the temperature than for the tension coefficient, because there is here no assumption so questionable as our neglect of $(\partial\alpha/\partial T)_\theta$ in computing the tension coefficient.

Comment seems to be called for in one particular with regard to the values found for lithium. The calculated atomic radius is so small that the spheres of influence do not overlap, and the effective section of the channels is not in appearance like that shown in Fig. 5. I have therefore made a more exact computation for this case, putting as the fundamental equation

$$\text{Area of channel} = L^2 - 2\pi(a + \alpha)^2.$$

The analysis may be carried through on the exact lines of the above, except that instead of linear equations there are quadratics to solve. The result differs by only a few per cent. from that found by the simpler method, and it does not seem worth while to reproduce it. The essential feature in determining the result is the variation of the channel as c^2. It is also to be noticed that the values found for the radius of antimony justify our assumption of the rounded cube shape.

In connection with the small value of the effective radius of lithium as compared with the distance between atomic centers in the metal, it is interesting that Born[22] has recently arrived at a result of the same order of magnitude for the diameter of the lithium ion in solution. His value for the effective radius is 0.45×10^{-8} cm. against 0.62×10^{-8} cm. calculated above. Born states that the nature of his approximations is such that his result is small rather than large.

Our picture of the mechanism has been crude in the following particulars, among others. In the first place the assumption of the quantum theory of solids, which is at the basis of the formulas for the variations of α and ν, that the entropy is a function only of ν/θ, is probably not exact, and at any rate should have more careful verification. In the second place, Lindemann's formula for the frequency in terms of the melting

[22] M. Born, ZS. Elektrochemie, 26, 304, 1920.

temperature is known to be only an approximation for a number of substances. Thirdly, our assumption that the atoms act as if possessing a well-defined bounding surface of surface of definite shape can only be an approximation. In the case of lithium this approximation would seem to be particularly rough when one considers the atomic structure of lithium in terms of a nucleus and only three surrounding electrons. In fact, it is most difficult to see how the atom of lithium can have such a symmetry as to compel a crystal edifice of space centered cubic symmetry.

In view of the roughness of many of the assumptions it seems to me that the agreement of the observed with the computed values is as close as could be expected, and indicates that our picture of the mechanism is correct in the essential features. It is to be remembered that, so far as I know, there has been no previous attempt to account for the tension coefficient of resistance, and also that there has been no account given of the departure of the temperature coefficient from exact equality with $1/\theta$.

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A GRAPHICAL STUDY OF THE STABILITY RELATIONS OF ATOM NUCLEI.

By William D. Harkins and S. L. Madorsky.

Synopsis.

Graphical Study of the Electrical Properties of Atomic Nuclei and their Relation to Stability.—The properties considered are: P the number of positive electrons in the nucleus, which is taken to be numerically equal to the atomic weight, M the net positive charge which is equal to the atomic number, N the number of negative electrons which is equal to $(P - M)$, $[(N/P) - \frac{1}{2}]$ the excess of the relative negativeness N/P over the minimum $\frac{1}{2}$, and n the isotopic number which is equal to $(P - 2M)$ and also to $(N - M)$. The relations between each of these five quantities and each of the others for the various atomic nuclei are shown in ten two-dimensional plots which clearly bring out the stability relations and are of particular interest because of the limited region in each plot where atoms are found. Except in the case of hydrogen and of the helium isotope $P = 3$, N/P is never less than $\frac{1}{2}$ and M/P is never greater than $\frac{1}{2}$; in fact for 85 per cent. of the atoms composing the crust of the earth, both these ratios are equal to $\frac{1}{2}$ and n is equal to zero. As the atomic number, that is the net positive charge increases, the *relative negativeness necessary to stability* increases above $\frac{1}{2}$, more and more; that is, as alpha particles are added extra cementing electrons are required to overcome the increasing mutual repulsion of the positive units of the nucleus. An alpha ray transformation does not change n but increases N/P, while a beta ray change decreases n by 2 units and also decreases N/P; we therefore find that in each group of isotopes, the ones with larger values of N/P show greater beta-ray and less alpha-ray instability. Stability considerations also help explain the fact that the *number of isotopes* is on the whole smaller for the lighter atoms. The curves bring out other interesting relations. The number of isotopes is larger for even than for odd numbered elements, especially for $M \leqq 30$. Also for most atoms, M, n and P are either all even or all odd, but N is usually even. The curve for the *frequency of occurrence of atoms* as a function of n shows periodic maxima four units apart, while as a function of M (or of N) the periodic maxima are two units apart. These regularities make it possible to predict the existence of the more abundant isotopes of elements whose mean atomic weights are accurately known; for instance, in the cases of lithium and boron predictions made in 1920 were later verified by Aston and by Dempster.

In 1914 Rutherford [1] suggested that the hydrogen nucleus is the positive electron, and that the explanation of the fact that the helium atom has not quite four times the mass of the hydrogen atom, may be due to a "packing" effect. Less than a year later, Harkins and Wilson,[2] without knowing of this suggestion, published a careful study of the atomic weight relations of the elements, and developed what has since become known as the whole number rule, which is that pure atomic

[1] Rutherford, Phil. Mag., *27*, 494–5 (1914).

[2] Harkins and Wilson, Proc. Nat. Acad. Sci., *1*, 276 (1915); J. Am. Chem. Soc., *37*, 1367–1421 (1915).

species other than hydrogen, have atomic weights which are whole numbers, or very nearly whole numbers on the basis of oxygen as 16 or carbon as 12. This was stated in the form of an hypothesis: that the packing effect in the formation of helium from hydrogen amounts to about 0.77 per cent., but that the further packing which occurs in the formation of more complex atoms is so slight as to be obscured by the errors in the atomic weight determinations made on pure isotopes. The evidence of the chemically determined atomic weights of pure atomic species seems to justify the statement that while the atomic weight of free hydrogen is about 1.0078, the mean atomic weight of hydrogen in any complex atom is 1.000 ± 0.001.

Using these ideas as a basis, Harkins has developed a theory of nuclear stability and composition which indicates, among other important relations, that the elements fall into two classes which are on the whole essentially different in both stability and composition. These are: (1) Elements of even number, whose atoms are in general the more stable and the more abundant, and whose nuclei are mostly built up from alpha particles alone or of these together with negative electrons, whenever the nuclear system is not too complicated—that is when the atoms are light. Heavier atoms of this class have in general atomic weights which are divisible by two. (2) Elements of odd atomic number, whose atoms as a whole are less stable and less abundant, and contain in general three (sometimes one or two) hydrogen nuclei in addition to the alpha particles which constitute the greatest part of their composition. It was pointed out that the magnitude of the packing effect is likely to be different for the additional hydrogen nuclei from that found in the alpha particle. In general the atomic weights of pure atomic species of this class are odd numbers. The number of isotopes of elements of even atomic number is in general considerably larger than for elements of odd atomic number.

The atoms may be classified in a different way as (*A*) those of low atomic number (up to 28) which are in general by far the more abundant, and presumably the more stable. The number of isotopes for these elements is in general small. The atoms of elements (*B*) of high atomic number (heavy atoms) are rare, and presumably less stable than those of the light elements, but the number of isotopes (especially for the elements of even atomic number) is much higher.

If the nuclei of atoms are built up from positive and negative electrons, as indicated by the theory, it is easily seen that the number of particles involved is so great, for example 232 positive and 142 negative electrons, or 58 alpha particles, as to make the mathematical treatment of the

stability relations extremely difficult, especially since practically nothing is known concerning the laws of force or of the dimensions or form of the electrons in the nucleus. It seems worth while to make a simple beginning in this direction by plotting graphically the data now known which have a bearing upon the stability of atom nuclei, making use of such variables as seem to be related to this property.

Notation.

P atomic weight, or number of positive electrons.
M atomic number, or positive charge on nucleus.
N $P-M$, or number of negative electrons in the nucleus.
n Isotopic number.
p a positive electron.
e a negative electron.
a an alpha particle.
pe a neutron.

Variables Related to Atom Nuclei.

Two important variables related to the properties of the atom are the atomic weight (P) determined experimentally by chemical methods or by the use of positive rays, and the atomic number (M), which is also determined experimentally. This has been done by the use of the x-ray method of Moseley, and also by the independent method of noting the position of the element in the periodic system of Mendelejeff, which is simply a classification of the elements according to their properties as determined experimentally. The difference of two experimentally determined numbers (N) is also an experimentally determined number. In an exposition of the stability relations two additional dependent variables have been found to be of great convenience. These are the ratio N/P, which may be designated as the *relative negativeness* (presumably of the nucleus), and the isotopic number (n), which specifies the number of an isotope. The isotopic number may be defined as equal to $P - 2M$, so it may also be determined experimentally.

Since the mass and positive charge of an atom seem to be always associated, the term nucleus will be used to refer to that part of the atom which has these properties. The five variables listed above may be assumed to refer specifically to this part of the atom. As only two of the variables are independent, it is obvious that all of them may be represented on a single plane diagram, but, since in such a diagram only two of the axes are found to be at right angles to each other, it is necessary to use rectangular axes for each pair of variables if the relations which

[1] Obviously P/N may be used as the relative positiveness.

exist are to be made sufficiently obvious. In this way ten two-dimensional diagrams are obtained (Figs. 1 to 10).

Of the five variables under discussion only one, N/P, involves the ratio of two others. The other four give rise to six two-dimensional plots (Nos. 1, 2, 3, 8, 9, 10), each of which has the remarkable property that on it *constant values* of every one of the *five* variables, including N/P, are represented by *straight lines*. While this is obviously true of any set of whole number variables defined as these four are, independently of any atomic relationships, the importance of the diagrams consists in the fact that they give a good exposition of the elementary stability relations of complex nuclei. The characteristics of the ten two-dimensional plots are listed in Table I.

TABLE I.

Outline of the Ten Two-Dimensional Plots of the Variables P, M, N, n, and N/P, together with Equations representing Constant Values of the Variables.

(The ratio N/P is represented by R, and $(N/P) - 0.5$ by R'.)

Figure.	Independent Variables.	$R = k$, $R' = k'$.	$N = k$.	$P = k$.	$M = k$.	$n = k$.
1	P, N	$N = PR$	$N = k$	$P = k$	$N = P - M$	$N = \frac{P+n}{2}$
2	M, P	$P = \frac{2M}{1-2R'}$	$P = M + N$	$P = k$	$M = k$	$P = 2M + n$
3	M, N	$N = \frac{M(1+2R')}{1-2R'}$	$N = k$	$N = P - M$	$M = k$	$N = M + n$
4	M, R'	$R' = k'$	$R' = \frac{N-M}{2(N+M)}$	$R' = \frac{P+2M}{2P}$	$M = k$	$R' = \frac{n}{2(n+2M)}$
5	P, R'	$R' = k'$	$R' = \frac{2N-P}{2P}$	$P = k$	$R' = \frac{P-2M}{2P}$	$R' = \frac{n}{2P}$
6	N, R'	$R' = k'$	$N = k$	$R' = \frac{N}{P} - 0.5$	$R' = \frac{N-M}{2(N+M)}$	$R' = \frac{n}{2(2N-n)}$
7	n, R'	$R' = k'$	$R' = \frac{n}{2(2N-n)}$	$R' = \frac{n}{2P}$	$R' = \frac{n}{2(2M+n)}$	$n = k$
8	M, n	$n = \frac{4R'M}{1-2R'}$	$n = N - M$	$n = P - 2M$	$M = k$	$n = k$
9	P, n	$n = 2PR'$	$n = 2N - P$	$P = k$	$n = P - 2M$	$n = k$
10	N, n	$n = \frac{4R'N}{1+2R'}$	$N = k$	$n = 2N - P$	$n = N - M$	$n = k$

Note.—All of the fifty lines for constant values in the ten figures are straight except eight, as can be seen from the equations.

It should be noted that the position of the actinium series in these ten plots is in accord with the relations of this series as they have been given by Soddy; the actual relations being undetermined as yet. According to E. Q. Adams the atomic weight of actinium is an odd number, and that lead from actinium has an atomic weight of 207. This would fit in with the general system fully as well or even better than the scheme proposed by Soddy. Adams' system would be represented if each symbol for an element of this series were to be raised by *one isotopic* number, the atomic number being kept the same.

1. *P*, *N* Plot, and the Isotopic Number.

The remarkable feature of the plot which represents the number of negative electrons on the Y axis, and the number of positive electrons on the X axis is shown by the line with a slope of 1/2 which extends to the right from the origin. In no case is the point which represents the position of any species of complex atoms below this line, though hydrogen, and Rutherford's helium isotope of mass 3 lie below it. However the former of these two is simple, and the latter has not been found to exist as an atomic species. It is of extraordinary interest that 85 per cent. of all of the atoms in the surface of the earth, and 79 per cent. of the atoms in the meteorites are represented by points which lie exactly on this line, on which the relative negativeness to positiveness of the atom nuclei is just as 1 to 2, or 1/2. Since the formula of any nucleus of this type is $(p_2e)_M$, or $a/2$ it has been suggested by Harkins that the group p_2e may be the most fundamental group concerned in atom building. However, since for more than 99.9 per cent. of the atoms of this formula M is an even number, it seems that, if this group exists, it is very unstable with respect to aggregation, and unites with itself to form groups of the formula $(p_2e)_2$, which are alpha particles.

All of the pure atomic species which are represented by points which lie above this line, lie on 54 lines parallel to it; whose slope is therefore also 1/2. These are lines of constant isotopic number. The isotopic number of the line of this slope which passes through the origin is zero, the isotopic number of ordinary uranium is 54. The space available for these lines in the diagram is so small that only the zero line is represented. On this plot the lines of constant atomic number have a slope of 1 to 1, or along such lines N must increase by 1 if P increases by 1, so the formulæ of isotopic nuclei differ by one or more neutrons of the formula pe. Thus the nucleus of any atom is represented by the formula $(p_2e)_M\,(pe)_n$, where n is the *isotopic number*. The chart of the radioactive elements shows, as is evident from the formula of the alpha particle

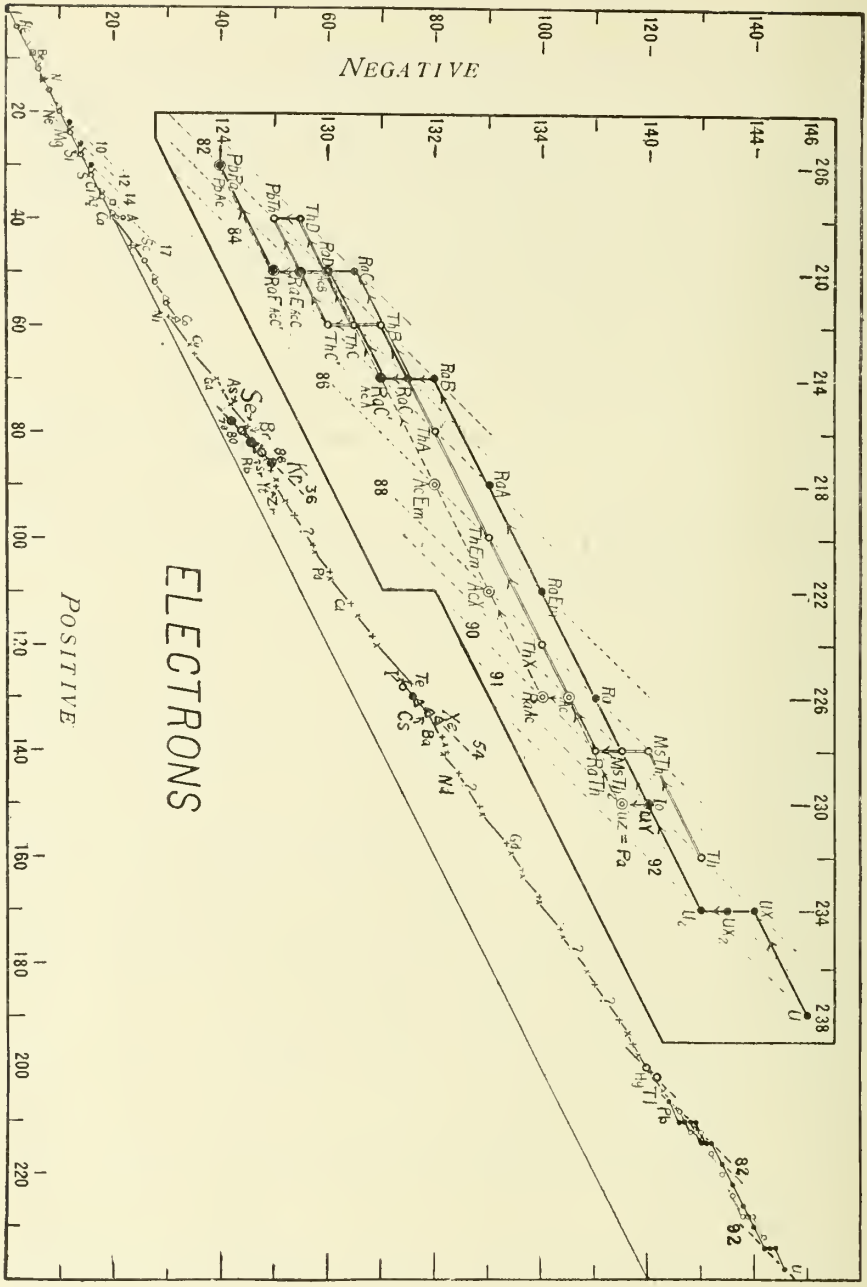

Fig. 1.

Plot of the total number of negative and positive electrons in atom nuclei. Isotopes ($P - N$ = a const.) lie on lines (dotted when they are given) which have a slope of 45°. Members of the helium-thorium series are represented by open circles, of the metaneon-uranium series by circles which are inked in, the lithium series by triangles, and metachlorine (37) by a square. Note that the elements of the helium-thorium series from helium to calcium, and the radioactive elements in any series during successive alpha disintegrations, lie on lines which have a slope exactly equal to 0.5.

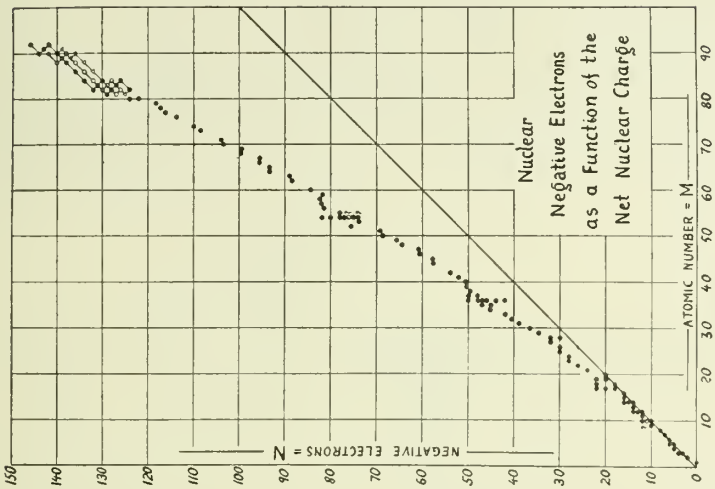
Nuclear
Negative Electrons
as a Function of the
Net Nuclear Charge
NEGATIVE ELECTRONS = N
ATOMIC NUMBER = M

Fig. 3.

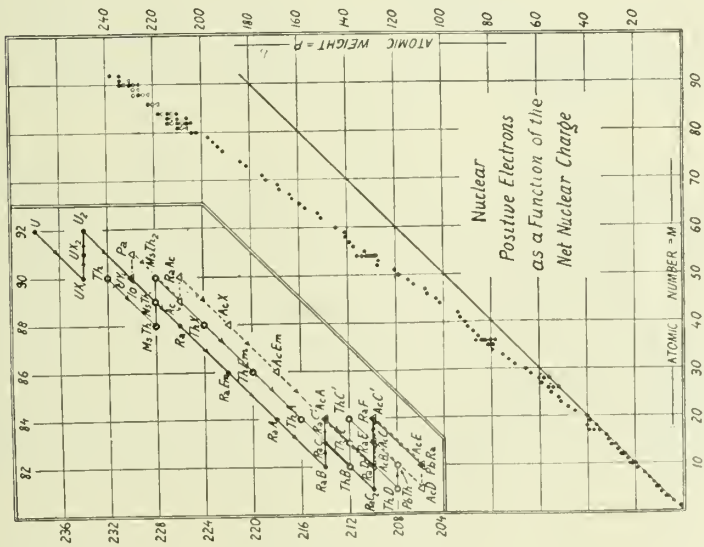
Nuclear
Positive Electrons
as a Function of the
Net Nuclear Charge
ATOMIC WEIGHT = R
ATOMIC NUMBER = M

Fig. 2.

$(p_2e)_2$, that during a series of alpha disintegrations the isotopic number remains constant. Lines of beta disintegration are lines of constant P, along which the number of positive electrons remains constant. The lines of constant N/P radiate from the origin. Most of the other features of this plot are shown more plainly in some of the other diagrams.

The isotopic number is that number which must be added to twice the atomic number to give the atomic weight, and represents the number of neutrons in the nucleus in excess of the formula $(p_2e)_M$. The value of the isotopic number is given by the following equations developed by Harkins:

$$n = P - 2M, \tag{1}$$

$$n = 2N - P, \tag{2}$$

$$n = N - M. \tag{3}$$

As the atomic number increases the isotopic number also increases in general, or the ratio of N/P increases above its minimum value 1/2.

2 AND 3. M, P, AND M, N PLOTS.

In the plot on which M is given on the X, and P on the Y axis, the most abundant atomic species lie on a line with a slope of 2 to 1, or in such atoms the atomic weight is twice the atomic number. All other species of complex atoms are represented by points which lie above this line. It is obvious that the ordinates are given by the equation:

$$P = 2M - n.$$

Fig. 3, which gives the atomic number on the X, and the number of nuclear negative electrons, on the Y axis, resembles Fig. 2 very much, the difference being that the line of minimum slope has the slope 1 to 1. Any point on one of these diagrams is the same number of units above the line of minimum slope on one diagram as it is on the other. This number of units gives the isotopic number, or the number of neutrons present in excess of the formula $(p_2e)_M$. The great simplicity of the relations in Figs. 1 to 3 is due to the fact that the minimum value of N/P which is 1/2, gives the minimum value of P as $2M$, and the minimum value of N as equal to M, since $M + N = P$, or $(M/P) + (N/P) = 1$.

4, 5, AND 6. M, P AND N, ON THE X AXIS; $N/P - 0.5$ ON THE Y AXIS.

Figs. 4, 5, and 6 are very much alike, since the ordinates are the same on all of the three plots. The abscissæ are different, but are very nearly proportional to each other, since M and N are not very different, and P is nearly twice M. Of the three only Fig. 4 will be discussed in detail. In this the *relative negativeness* of the nuclei is given on the Y, and the

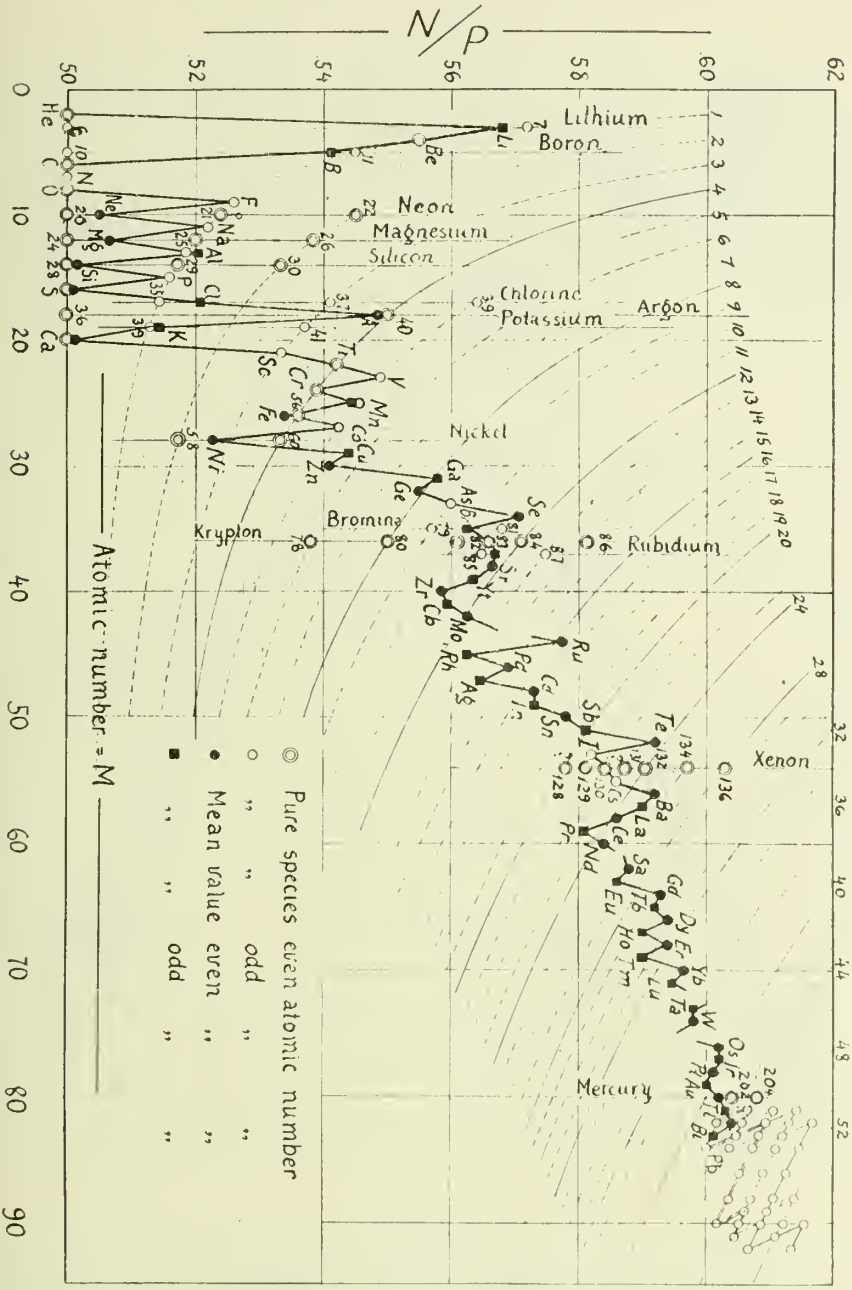

Fig. 4.

The ratio (N/P) of negative to positive electrons in atom nuclei as a function of the atomic number (M). $y = N/P - \frac{1}{2}$; $x = M$.

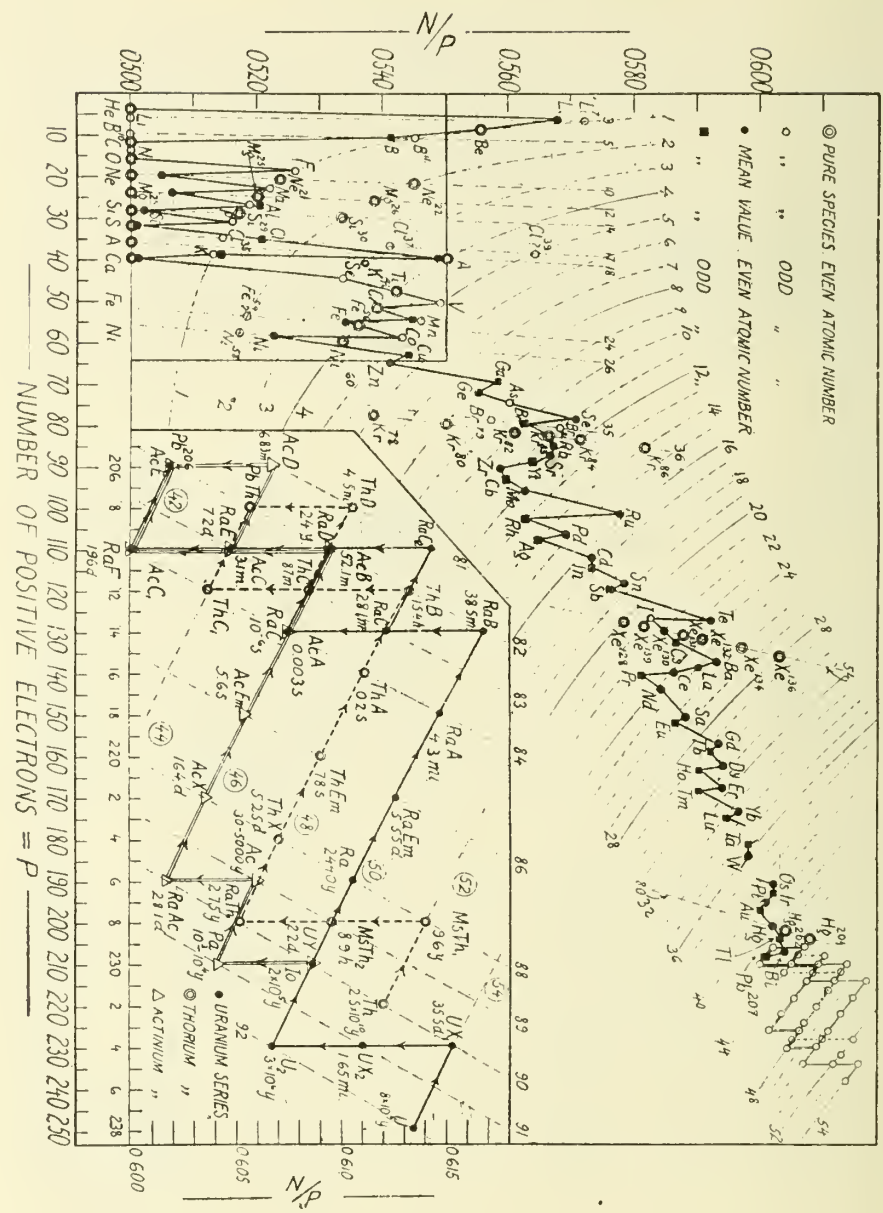

Fig. 5.

Plot showing the ratio of the number of negative to positive nuclear electrons on the Y-axis, and the number of nuclear positive electrons on the X-axis. Atomic species of zero isotopic number lie on the horizontal line $N/P = 0.5$, which is taken as the X-axis of the plot. The isotopic numbers of the other atomic species are given by the numbers of the equilateral hyperbolas.

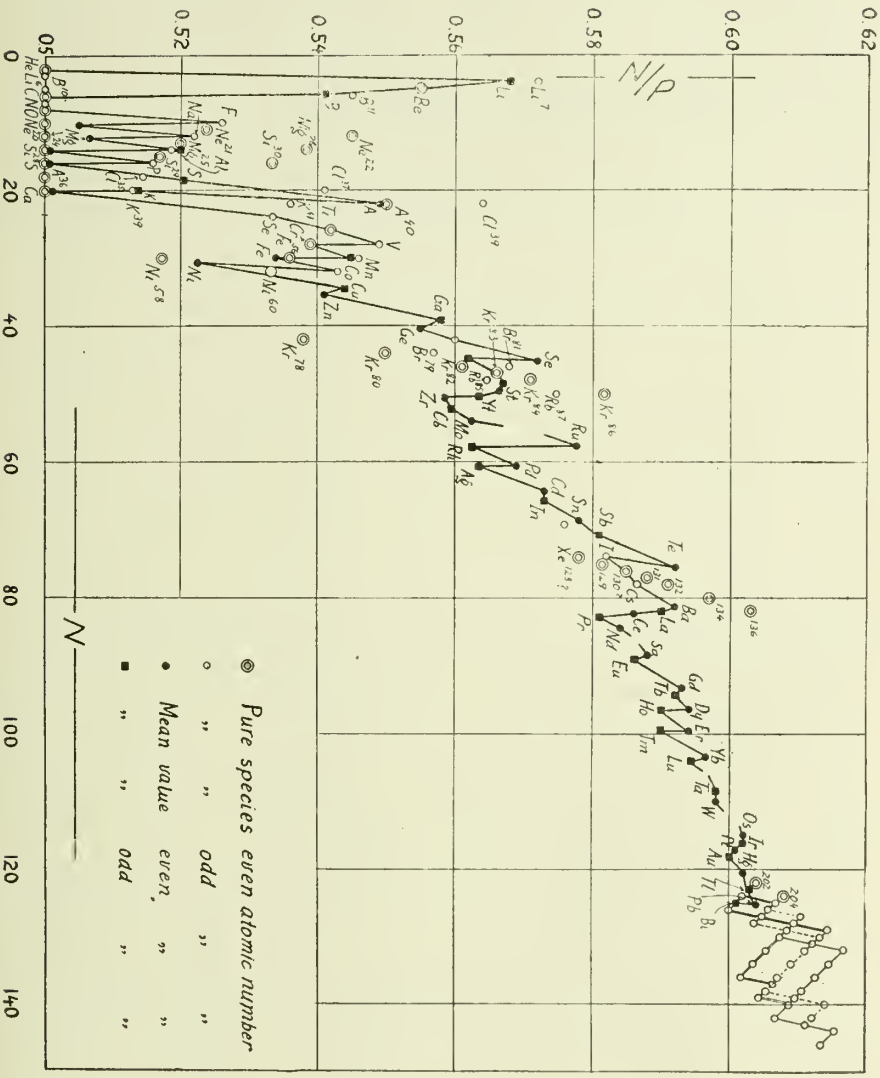

Fig. 6.

Ratio (N/P) of the number of negative to positive electrons in atom nuclei as a function of the number of negative electrons (N).

net positiveness on the X axis. The hypothesis that *the net positive charge on the nucleus exerts a certain self-repulsion, and that this self-repulsion increases with an increase of the charge, provided the relative negativeness of the nucleus remains constant,* has been developed by Harkins.[1] *Stability is secured as the net positiveness increases, by an increase in the relative negativeness.* This is obtained in nuclei built up of alpha particles alone, by the introduction of negative electrons (cementing electrons), used in cementing the alpha particles together. Only cementing electrons are given off in beta disintegrations of the radio-active elements. To a smaller extent an increase in the relative negativeness may be brought about by the addition of groups in which the ratio of N/P is greater than 1/2. Such groups are p_2e_2, p_3e_2, and pe.

Evidence that the relative negativeness (or positiveness) plays an extremely important part in determining stability is found in the relations of the radioactive elements (lower right-hand corner of Fig. 5).[2] This shows plainly that *if atoms of constant net positiveness* are considered, it is found that as the nucleus becomes more negative in the relative sense, the instability with respect to the emission of negative electrons increases (beta period decreases), and the instability with reference to the emission of positively charged particles decreases (alpha period increases). This indicates that even in the closely packed nucleus, unlike charges attract, and like charges repel, or the sign of the effect is the same as at greater distances. Nicholson and other theorists have assumed, without any evidence for their point of view, that this is not true. When radioactive elements of different atomic numbers are compared, no such relation is found, and it is seen that there is a strong indication that the cementing electrons are arranged in pairs, and the alpha particles in groups of varying number, but averaging about four.

The isotopic lines in Fig. 4 have very nearly the form of rectangular hyperbolas, their equation being $2y(2x + k) = k$, in Fig. 6 their equation is $2y(2x - k) = k$, and in Fig. 5 they are rectangular hyperbolas, $xy = k/2$. In these equations k represents the isotopic number. The stability relations may best be expressed by considering one of these lines, for example that for isotopic number 1. The most abundant elements, aluminium, sodium, and Mg_1^{25}, lie near the cusp of the curve. In either direction along the curve, as either N/P or M, that is as either the relative negativeness or the net positiveness, increases, the abundance of the atomic species decreases. Going in either direction along any

[1] Harkins, J. Am. Chem. Soc., *42*, 1971–3 (1920).

[2] Fig. 4, if it gave an enlarged diagram of the radioactive elements, would show this even more simply, since the lines of constant atomic number are vertical, but the two plots are so nearly alike that it seems unnecessary to duplicate this part of the figure.

one of these lines, starting at the position of maximum stability of the nucleus, the instability of the atoms decreases so greatly that after a certain, not very great distance is traversed, no atom is capable of existence for any appreciable time.

It has been shown by Harkins that the nuclear properties are to a considerable extent periodic, the periodicity being between elements of even and odd atomic number. Figs. 4, 5, and 6, indicate that among the light elements (atomic numbers 2 to 32) the mean value of the *relative negativeness* is much higher for elements of odd than for those of even atomic number (except in the case of three transition elements, Be, A, and Sc). Curiously enough, among the elements of higher atomic number, the relative negativeness is in general considerably higher for the elements of even atomic number, since all of the high peaks, and most of the minor ones as well, represent elements of even atomic number. In all of these three figures the lines of constant atomic weight (P) slope more to the left than those for constant atomic number (M), while the lines representing a constant number of negative electrons, slope still more to the left. This is shown by the equations given in Table I.

7. n, $(N/P) - 0.5$ Plot.

Fig. 7 illustrates the increase of the relative negativeness of the nuclei as the isotopic number increases. All of the extremely abundant atomic species, with the exception of iron and aluminium, are represented by the *point* N/P equal to 0.5, with an isotopic number zero. The region of highest stability has very nearly the form of a parabola, and along any isotopic line the stability decreases on passing vertically higher or lower. As an example the lines showing the net nuclear charge as 92, the number of positive electrons as 238, and the number of negative electrons as 146, which are the values for ordinary uranium, are given. These lines indicate that for a nucleus with any of these three properties, represented by relatively large numbers, to exist, the isotopic number must increase to a sufficiently high value (about 54) to cause the value of the relative negativeness to become sufficiently high (about 0.614) that the repulsion due to large net positiveness may be overcome by the high relative negativeness.

The diagram in the lower right-hand corner of Fig. 7 indicates that during alpha disintegrations the isotopic number remains constant, while the relative negativeness (N/P) increases slightly. After several changes the nucleus becomes so negative in the relative sense that positively charged particles no longer leave it, but negative electrons are shot off. Each beta disintegration lowers the isotopic number by

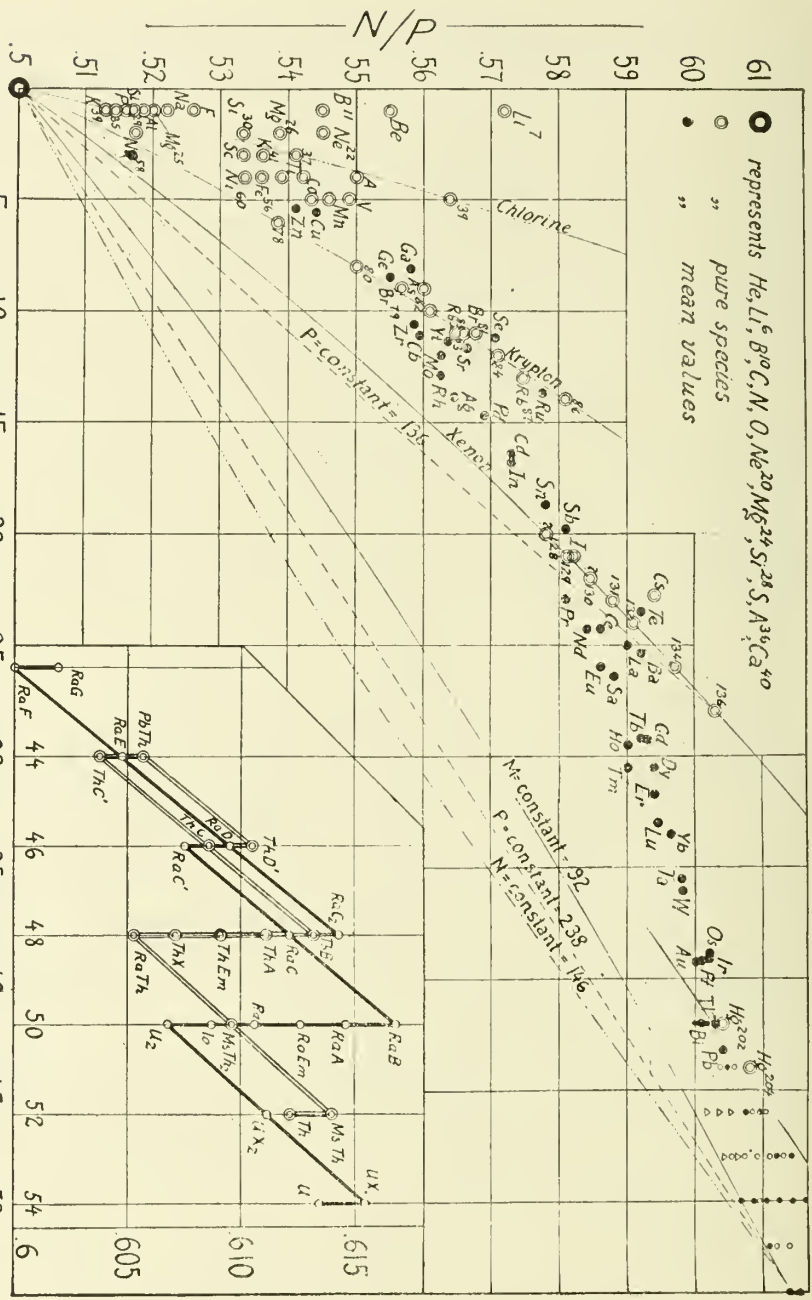

Fig. 7.

Ratio (N/P) of the number of negative to positive electrons in atom nuclei as a function of the isotopic number (n).

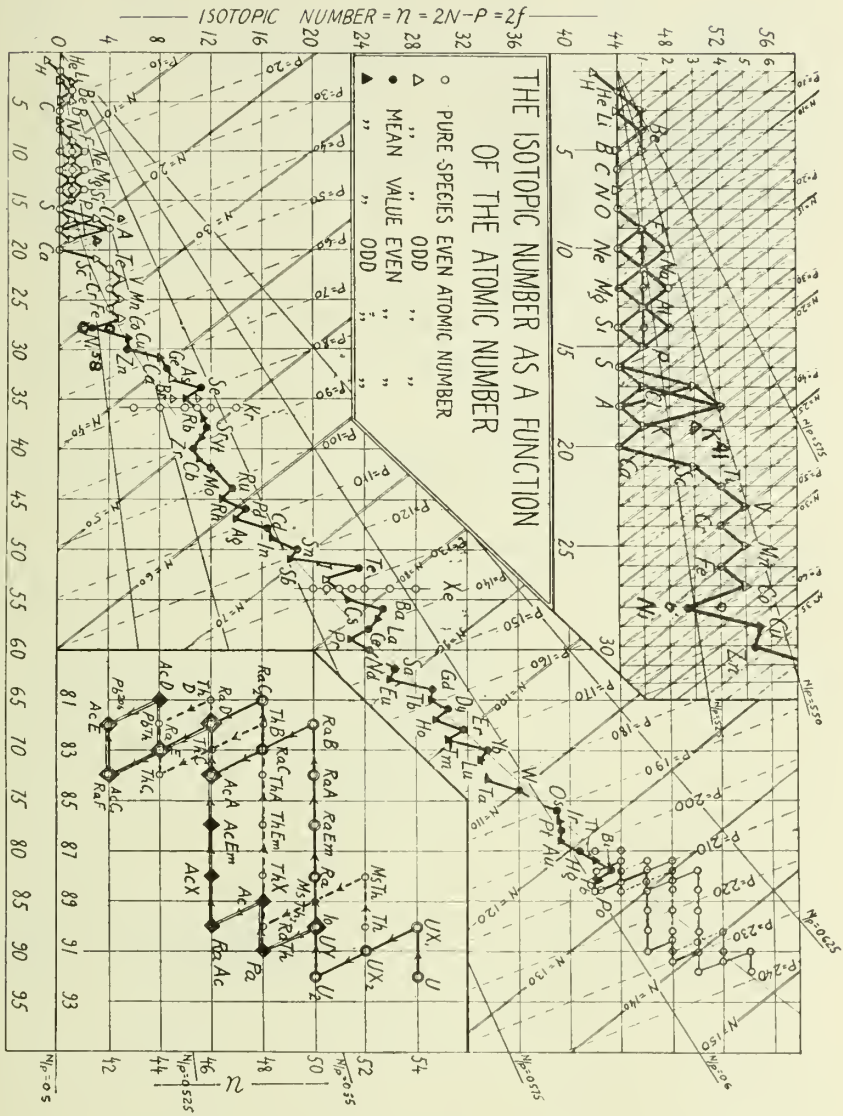

Fig. 8.

On this plot constant values for (1) the net positive charge on the nucleus, M; (2) the number of hydrogen nuclei or positive electrons in the nucleus, P; (3) the number of nuclear negative electrons, N; (4) the isotopic number, n; and (5) the ratio N/P, are all represented by straight lines.

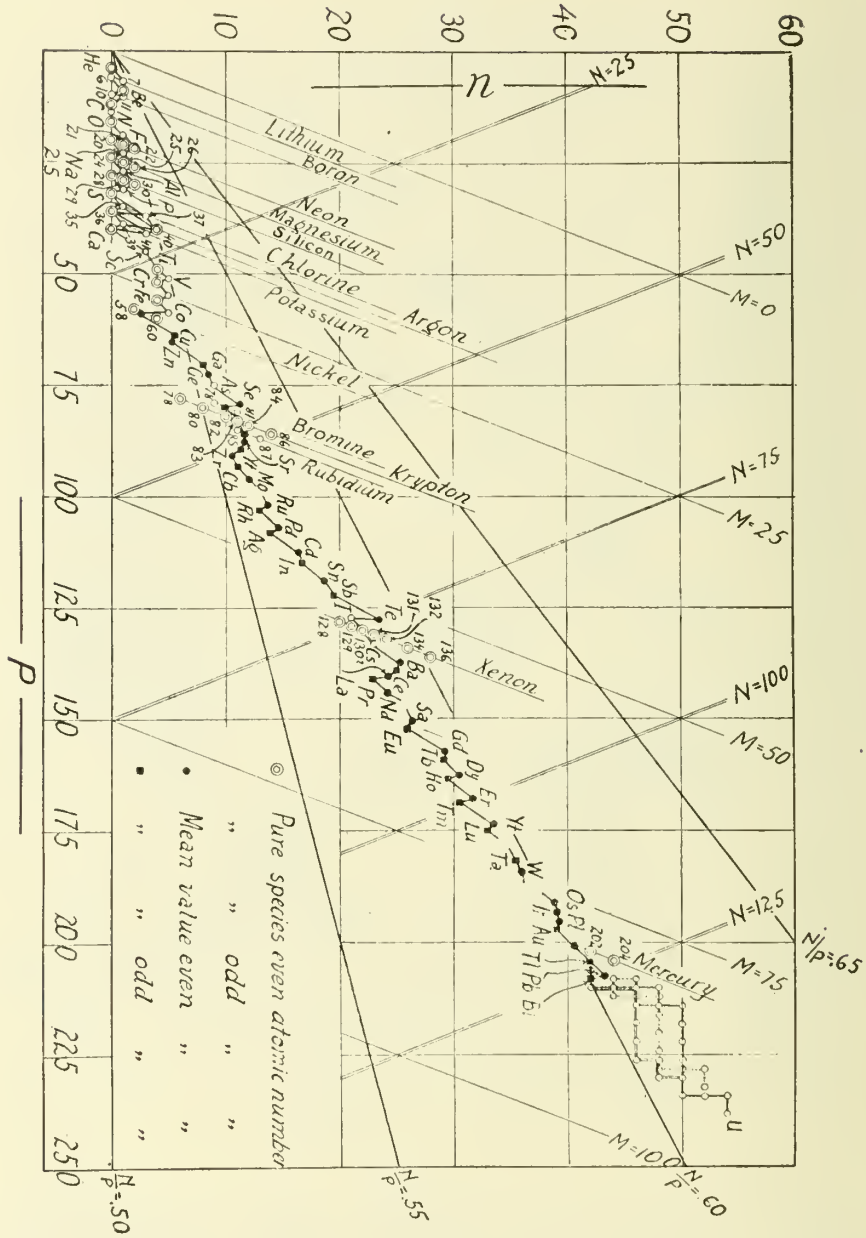

Fig. 9.

Isotopic number as a function of the number of positive electrons.

two, and in this region decreases the relative negativeness slightly more than two alpha disintegrations. It may seem strange that the loss of one negative charge changes the numerical value of the ratio N/P more than two losses of doubly charged positive particles, but the reason for this is obvious, since the loss of an alpha particle decreases both P and N. It is apparent that beginning with uranium, 27 beta changes would be sufficient to bring the plot to the origin, independently of the number of alpha changes, so this is the highest number of beta changes of this type possible for any known atom.

8, 9, and 10. M, P, or N on the X Axis, n on the Y Axis.

Figs. 8, 9, and 10 represent the isotopic number on the Y axis. All of them have the property that constant values of all of the five variables are represented by straight lines; four, P, M, N, and n, by sets of parallel straight lines, and N/P by lines radiating from the origin. The heavy lines in the radioactive region indicate the paths of the decompositions, but in the remainder of the diagram are only intended to bring out the position of the region of highest stability, which takes on very nearly the form of an hyperbola. A part of this figure has been considerably enlarged, and is shown in Fig. 11, which will serve to indicate the relations more clearly.

In figure 11 the lines for four of the variables, P, N, M, and n, all meet at every corner. Each such corner corresponds to the existence of a *possible* isotope, but not every corner corresponds to a condition of stability. From the general theory already presented it is to be expected that most of the corners which are filled will represent an *even number* of negative electrons. This means that when the atomic number (M) is even, the isotopic number (n) is also even, and when the atomic number is odd, the isotopic number is also odd. *Thus in general the atomic number, isotopic number, and number of positive electrons, all match in the sense of oddness or evenness*, that is all of these numbers are either even, or else they are all odd. In the range of this figure, 3 out of the 31 atomic species thus far found, do not follow this rule. The secondary relation here revealed is that in a small fraction of the known atomic species P and N are both odd together. Only in extremely exceptional cases (less abundant isotopes of Li and B) is N odd, and P even.

Figure 11 has exactly the characteristics which it would have if across it had been plotted the tracks of four radioactive disintegration series, and it gives ample evidence that the light atoms from carbon to zinc as well as the heavy atoms are built up from alpha particles of mass 4, for along each isotopic line the atomic number jumps by 2 and the atomic weight

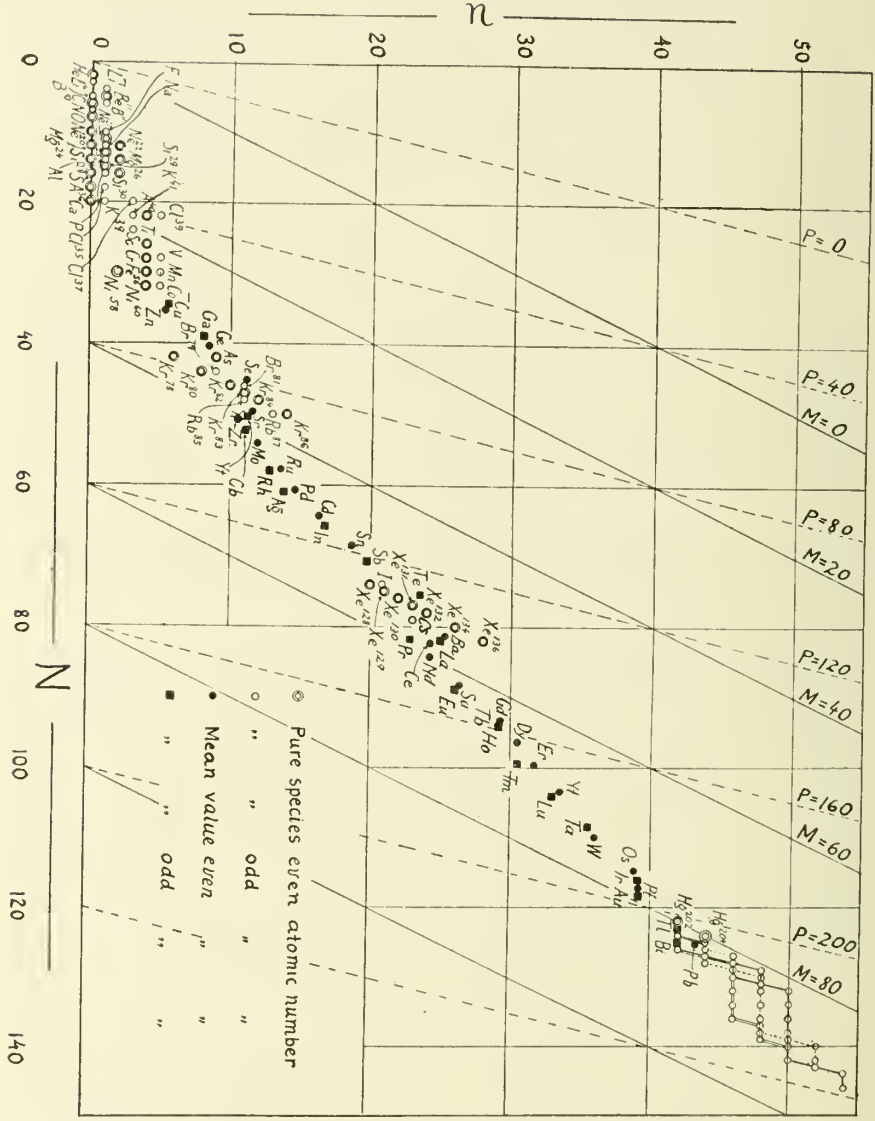

Fig. 10.

Isotopic number (n) as a function of the number of negative electrons (N).

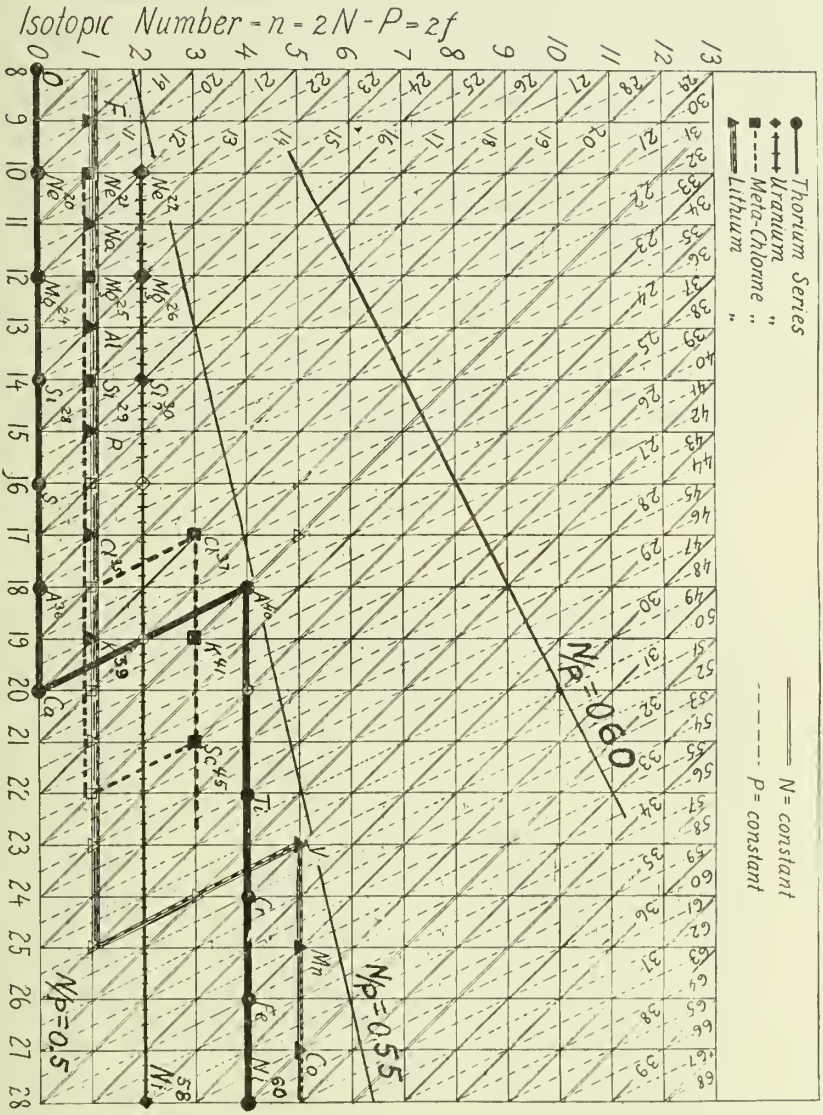

Fig. 11.

(Enlarged section of Fig. 8.) Isotopic number as a function of the net nuclear charge (M)

by 4. Only between fluorine and phosphorus do two of these series become intermingled. Out of the 14 atomic species depicted as belonging to the Helium-Thorium Series, only two remain undiscovered. One of these, K^{41}, probably does not exist in quantities large enough to be easily discovered. The other is Ca^{44}. The form of such a plot is determined by the stability relations of the atoms. The figures of this paper suggest that the light atoms, as well as the heavy ones, both build up, and disintegrate. The ratio N/P changes much more markedly with the isotopic number among the light than among the heavy atoms, so the range of the isotopes in terms of the isotopic number or atomic weight, is much less when the atomic number is low. It is of interest to note that in Fig. 11, while the value 0.55 for the value of N/P is practically attained three times, in no place is it exceeded. While in this range atoms with values of N/P higher than this limit may be discovered, it is now apparent from the atomic weights and the general relations involved, that no such atomic species will be at all abundant.

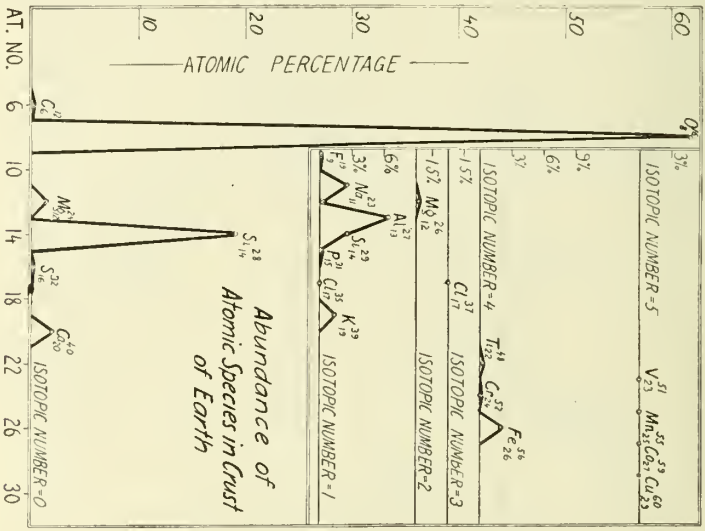

Fig. 12.

Shows the periodic variation in the abundance of the atomic species of each isotopic number.

That the abundance of the atoms of any isotopic number is periodic, is shown by Fig. 12. The abundance is greatest for isotopic number 0, and decreases gradually to a minimum in isotopic number 3, rises to a secondary maximum in isotopic number 4, and again decreases. Thus there is also a periodic variation of the abundance of the atoms in the isotopic numbers, which gives a maximum with each fourth isotopic

number. While these maxima probably become much less prominent as the atomic number increases, their prominence in the range of low atomic numbers is strongly suggestive that the periodicity by 4 is due to the fact that 4 is the mass of the alpha particle.

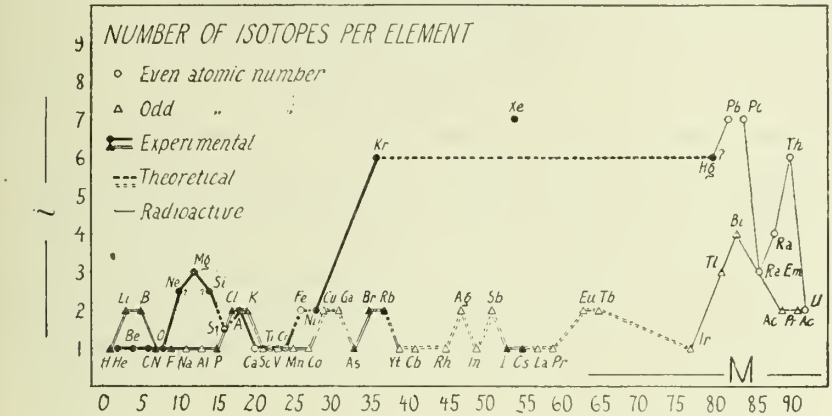

Fig. 13.

Approximate number (i) of isotopes per element.[1]

[1] This figure plots the number of isotopes per element thus far discovered, using inked-in symbols. For elements whose isotopes have not been determined a rough estimate of the probable number is given. This number is based upon the assumption that the chemical atomic weight is entirely exact. In so far as this assumption is not justified, the number of isotopes predicted cannot be expected to be correct; and it is well known that many of the chemical atomic weights are very much in error. This is illustrated by the case of antimony, the atomic weight of which has been changed more than a unit by the most recent determinations. The number of isotopes in neon and silicon is plotted as 2.5, an impossible number, to indicate that Aston's experimental determinations are indefinite, giving in each case two isotopes, with a third doubtful. While the number of isotopes plotted for the radioactive elements is greater than for the preceding elements, this is only because the experimental means used for their detection is much more delicate. While Aston was able to find only one atomic species for sulphur, the chemical atomic weight indicates that sulphur consists of at least two isotopes. To show the relations properly the plot should be three-dimensional, and should give the abundance of each isotope. For example, in the two-dimensional diagram lithium, with only 6 per cent. of the higher isotope, is given the same rating as chlorine with 23 per cent. and bromine with about 50 per cent., which gives a false impression unless these facts are kept in mind. The designation of indium, columbium, yttrium, lanthanum, and praeseodymium as consisting of only one isotope each, is probably without meaning, since in most of these the atomic weight is not known with sufficient accuracy as to give a basis for a definite prediction. On the other hand the atomic weights of silver and copper are known with sufficient precision as to justify the *prediction that each of these elements consists of two isotopes.* It is of course possible that three isotopes may exist, but the number of isotopes sufficiently abundant to be detected by the positive ray method in its present degree of sensitiveness, is in general not greater than two for elements of odd atomic number.

The most important feature of this plot is that it illustrates the fact that *the number of isotopes is in general much higher for elements of even than for elements of odd atomic number, especially for elements of atomic numbers greater than 30.* This is exactly in accord with the

Figure 13 shows the way in which the number of isotopes per element varies with the atomic number. It will be seen that the relations are exhibited most easily when separate curves are drawn for the elements of even and of odd atomic numbers. The lines represent only the most general form and not the details of the numerical relations.

While Aston did not find a higher isotope of sulphur, there is little doubt of the existence of such an isotope, which would have an atomic weight of either 34 or 33. Also there is little doubt that a higher isotope of calcium (possibly 42 or 44 atomic weight) and a lower isotope of iron (probably 54) exist. The stability relations contain specific factors of such importance that it is impossible to tell exactly the relative abundance of such isotopes. However it may be pointed out that Harkins predicted the existence of the 6 and 7 isotopes of lithium, the 10 and 11 isotopes of boron, and the 24 and 26 isotopes of magnesium without making a single error in the predictions, but failed to predict the existence of the 25 isotope of magnesium, for which the relations are much more specific.

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September 12, 1921.

predictions from the theory of the stability of atom nuclei as presented by Harkins in various papers published in the years 1915 to 1917. (It is of interest to note that the number of isotopes of element 30 (zinc) has just been found to be 4 by Dempster. Thus the number of isotopes increases exactly at the point predicted by Harkins in the year 1915.)

TIME AND PRESSURE MEASUREMENTS IN THE CORONA.

By Charles S. Fazel.

Synopsis.

Pressure Effects Due to the Corona Discharge in Dry Air.—The discharge took place from a fine wire inside a concentric tube. By means of a sensitive differential gage it was found that the pressure at the tube was 0.004 cm. of water higher than at the wire, *for both A.C. and D.C. discharges.* Studies made with a recording mica diaphragm gage showed that on starting the D.C. discharge the pressure rose gradually, reaching in about 1½ seconds a limiting value proportional to the current. The curves for A.C. discharges were the same except that superposed on the D.C. curves were periodic pressure changes with twice the frequency of the alternating voltage and with an amplitude of 0.3 cm. of water. When the wire was heated without the discharge, with either A.C. or D.C. current, the pressure curve took about 20 seconds to reach its limiting value and showed no periodic variations. If when the steady state was reached the corona discharge was started, the pressure either decreased to a lower limiting value, or increased to a maximum and then decreased to a limiting value lower than before or higher than before, depending on the voltage of the discharge. Evidently several effects are superposed in this case. The experiments show the existence of characteristic pressures in the corona in addition to the pressure due to the heating of the gas by the current through the wire.

Introduction.

THE gas pressure developed by the corona discharge has been studied by Farwell,[1] Kunz,[2] Warner,[3] Arnold,[4] and Tyndall.[5] Warner has shown that the corona pressure developed is proportional to the corona current. He has suggested that there was a true corona pressure distinct from that due to pure thermal effects and as an explanation has suggested the ionization theory. On the other hand, Arnold and Tyndall have contended that the effect was due to the heat developed.

The tube used by Tyndall had a diameter of 2.2 cm. and the wire of a diameter of .006 mm., while in Warner's work the tube was 4.5 cm. in diameter and the wire had a diameter of .019 cm. In addition the current used by Tyndall was of the order of magnitude of 10^{-3} amps. (unless there is a misprint in his article as some of his other data would indicate), while Warner used a current of magnitude of 10^{-5} amps. These differences could make the pressure evolution due to heat the

[1] Proc. A. I. E. E., 33, 717.
[2] Phys. Rev., 8, 28.
[3] Phys. Rev., 10, 483.
[4] Phys. Rev., 9, 93.
[5] Phil. Mag., 35, 483.

predominant factor in one case and the pressure due to the corona in the other.

The following experiments were undertaken to see whether there existed a characteristic corona pressure. The development of pressure due to heating the gas by the passage of the current could not be called such a pressure. But a pressure due to ionization or ionic wind would come under that class.

I. The Pressure Distribution Within the Tube.

In view of the possibility that the pressure might be due to the ionic wind the pressure difference between the walls of the tube and the wire was measured by a differential gage of the Wahlin[1] type. A special gage was constructed so that the columns over the liquids were as small as possible and the ratio of the cross sectional areas of the tubes was about one to ten.

One side of the gage was connected to the outside of the corona tube while the other was attached to a glass tube which could be moved in to the center of the tube. The connections from the tube to the gage were kept as short as possible. The gage thus read the difference in pressure between the walls of the tube and the neighborhood of the wire. Considerable difficulty was experienced until the air was dried very thoroughly by passage through sulphuric acid and calcium chloride. The presence of water vapor lowers the voltage at which an arc will form and tends to decrease the corona pressure difference.

With carefully dried air and the sensitive gage mentioned above a pressure difference between the wire and the tube of about .004 cm. of water was detected at 12,000 volts D.C. The walls of the tube were always at the higher pressure whether the wire was positive or negative. The apparatus was not sensitive enough to tell whether there was any difference in the magnitude of the pressure difference when the wire was positive or negative.

Tyndall[2] has calculated from Chattock's values for the mobility that the electric wind should give rise to a pressure difference of .003 cm. of water between the wire and the tube. It would therefore seem that the pressure just measured was due to the ionic motion.

Even with this difference it is still difficult to see how such a small air movement could accomplish the cooling which Tyndall attributes to it. The motion of the air due to this small pressure difference would last for a short time and could not produce very much cooling, especially on account of the small specific heat of air.

[1] Bull. University of Illinois Eng. Exp. Sta., No. 112, p. 25, 1919.

[2] Phil. Mag., 35, 264.

Fig. 1..

Fig. 3.

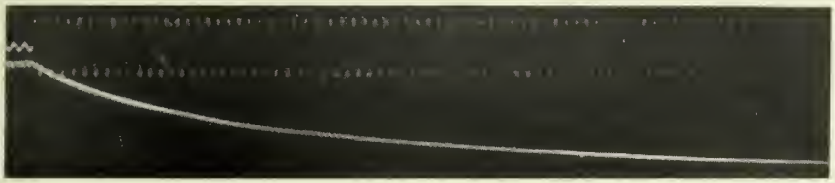

Fig. 4.

Fig. 6.

CHARLES S. FAZEL.

II. Corona with the Manometric Flame.

It would seem possible to distinguish between the corona pressure and the pure heat effects on the basis of the time taken to reach the steady state. In order to study this a corona tube was supplied with a sixty-cycle alternating potential of about twelve thousand volts. The outside of the corona tube was grounded to eliminate electrostatic effects. A connection was then made from the tube to a manometric capsule.

Using this apparatus a new phenomenon was observed. It was found that the flame showed a periodic pressure change of twice the frequency of the impressed electromotive force. By pinching the rubber tube connecting the corona tube with the capsule the vibrations of the flame stopped. Grounding the capsule and other parts of the apparatus produced no effect on the flame. A sample record is shown in Fig. 1. The upper is the pressure while the lower is a manometric flame attached to a telephone which carries part of the same current which actuated the transformer. For the lower flame the length of each spot of light represents a one hundred twentieth of a second (for the remainder of the cycle the flame is extinguished). It should be noticed from the upper flame that the pressure change in the corona tube is able to follow a frequency of one hundred and twenty cycles per second, which is much faster than any of the pressure changes observed before in the corona.

It was noticed that the flame was greatly affected on the make and break of the current. In fact it was often extinguished at these times if it was in its most sensitive condition. In order to investigate this phenomenon a pressure gage was built which would give readings of pressure rather than change of pressure with the time. The results obtained with this gage will be discussed later (Part III.).

The heating of the gas by an alternating current passed through the central wire was tried to see whether the alternating pressure might not be due to the alternate heating and cooling. With this arrangement the flame did not show any oscillations even though the wattage used was more than ten times that used in the corona.

In case the central wire was heated by the alternating current as above and at the same time the corona was put on the tube the flame behaved in exactly the same way as it did when the wire was not heated. That is, the flame showed a periodic pressure of twice the frequency of the impressed electromotive force. This indicates that the variations in the pressure depend on having a varying potential difference between the wire and the outside of the tube and not on the temperature of the wire nor in the variations of its temperature due to the alternations of the current.

With the same apparatus as used on the alternating current corona, the direct current corona was investigated for an oscillatory pressure. With the direct current on the corona tube no oscillations could be detected except irregular fluctuations with a period of about a second which were probally due to variations of the voltage of the machines. With the spark in series with the tube no oscillations could be detected using the flame and the rotating mirror.

III. Corona with the Pressure Gage.

The experiments described above with the manometric flame showed that there must be effects on the make and break of the current which could not be shown with this flame. In order to study these effects more fully a quick-acting recording pressure gage was constructed.

This gage consisted of a diaphragm of mica which was placed across the end of a corona tube having a wire which ran about seven-eighths of the full length. Attached to this mica plate was a silk thread held taut by a spring. A small mirror was supported on a vertical thread by one edge and the other edge was attached to a horizontal thread. Any motion of the mica diaphragm was thus transmitted to the mirror which gave a deflection of a beam of light. The gage as used gave a five-centimeter deflection for a pressure of one centimeter of water. The natural period of the gage as used in most of the experiments was in the neighborhood of 700 vibrations per second. The current in the primary of the transformer was recorded by an oscillograph. A diagram of the apparatus is shown in Fig. 2.

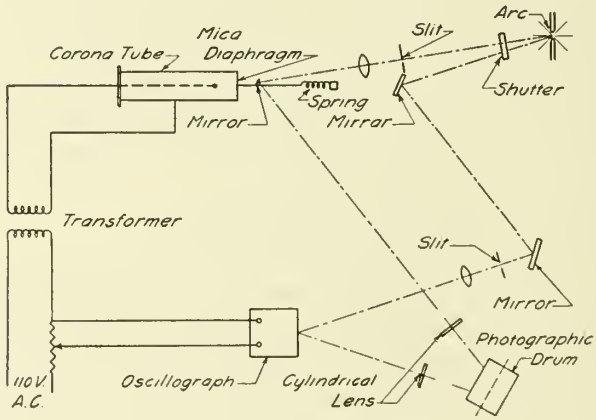

Fig. 2.

Using such a gage, Fig. 3, shows the increase in pressure in a corona tube when an alternating current of sixty cycles is thrown on. The

voltage is about nine thousand volts at the peak. The halo on the rising line is due to diffraction of the beam of light at the slit. The sine curve is the sixty-cycle wave representing the current. The record begins about one fourth of the distance from the left-hand side and reads right to left. There is some overlapping due to the shutter not being closed quickly enough.

It is evident that there are present the oscillations shown by the flame having half the period of the impressed electromotive force, but these are superimposed on a gradually increasing pressure which reaches a constant value in about a second and a half. There are two distinct types of pressure here, one which is able to follow variations of one hundred and twenty cycles per second, and another which requires more than a second to reach its value. The rapid pressure variations are such a large value that they cannot be the electric wind pressure. The "electric wind" pressure should have a magnitude of about .005 cm. of water while the alternating pressure change has been found to have a value of more than .3 cm. of water.

An attempt was made to study in greater detail the steady state of oscillation reached at the end of Fig. 3. This was done by the use of a thinner diaphragm and greater magnification which was obtained by decreasing the width of the mirror and increasing the distance from the mirror to the film. It was found that this brought the free period of the gage so near to the period of the oscillations which were being studied that satisfactory results were not obtained.

The variations in pressure which follow the breaking of the primary current of the transformer were studied and Fig. 4 shows the result. There is a slow dying away of the pressure which corresponds to the slow increase shown in Fig. 3. However, there is a new phenomenon as the oscillations persist with their original frequency and die out very slowly. These cannot be due to the natural frequency of the diaphragm or measuring system on account of the difference in frequency nor could it be the natural frequency of the electrical system as it would be in the millions of oscillations per second. This might be due to reverberation as the cylindrical wave—similar to a sound wave—would persist until its energy was absorbed by the walls. This point however requires further study.

IV. Heat Effects in the Corona Tube.

In order to study the effect of heat alone on the pressure development an alternating current was sent through the central wire and the increase of pressure observed. It was found that this pressure increase was so

slow that it could not be recorded on a photographic film with the apparatus at hand and so the results were obtained by visual observation. It was found possible to reproduce these observations within half a per cent., at the upper values and so the method was considered satisfactory.

Fig. 5 shows the curves for several different currents through the wire.

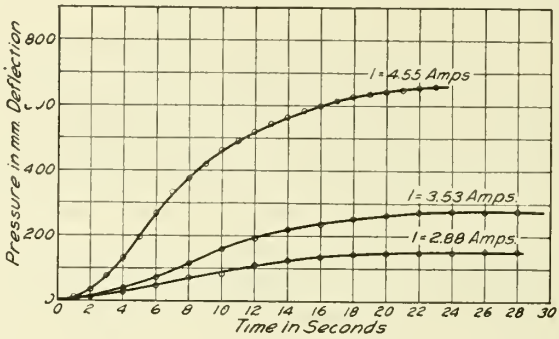

Fig. 5.

It will be seen that the maxima are not reached until the wire has been heated for more than twenty seconds, while Fig. 3 showed that in the alternating current corona the maximum is reached in less than two seconds. Further, the time required to reach the maximum does not depend upon the current to any marked extent. The maximum pressure reached depends on the current through the wire as would be expected. There is a marked difference in form of curves in Fig. 5 from those of Fig. 3. There would be no difficulty in distinguishing this type of pressure from the very rapid type shown in Fig. 1 and Fig. 3. It therefore seems possible to distinguish between the pressure due to the heat evolved and the pressure due to the corona.

V. Relation between Heat and Corona.

Tyndall[1] describes an experiment in which he had a tube with a wire heated by a current such as that used in the preceding experiments. After the pressure due to the heated wire had reached a steady value he threw on the corona and observed a pressure decrease. A similar experiment was performed recording the slow part by visual observations and the pressure changes when the corona was first put on by means of the recording pressure gage. The record of the pressure changes when the corona was first put on is shown in Fig. 6. The results of the whole experiment are shown in Fig. 7.

It is seen that as soon as the corona is thrown on there is a very quick

[1] Loc. cit.

increase in pressure followed by a slow decrease to another constant value below the original. Tyndall's failure to observe the initial increase may have been due to the use of a rather slow acting pressure gage, or to the relation between heat and corona.

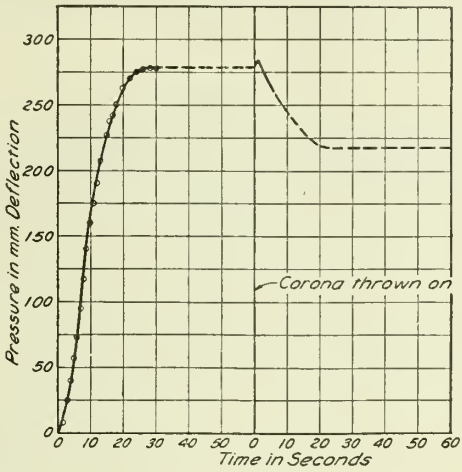

Fig. 7.

A study was then made of the maximum excursions on either side of the steady state by varying the voltage across the transformer. A number of records similar to Fig. 7 were made. The value of the sharp peak reached after the corona was thrown on, was plotted above the axis in Fig. 8 with the voltage of the transformer as abscissa. Likewise the

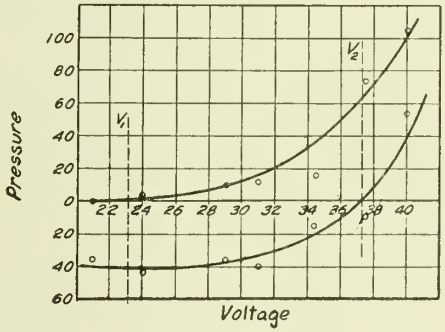

Fig. 8.

final pressure reached at the end of the experiment was plotted below the axis in Fig. 8.

From these curves it is seen that it is possible to find a voltage V_1, below which there is a decrease in pressure without any appreciable

initial increase. It is possible that Tyndall's experiments were conducted below this voltage. Between the voltage V_1 and V_2 there is an increase in pressure followed by a decrease to a value below the original pressure. Above the voltage V_2 the pressure increase is followed by a decrease but to a value above the original pressure. This shows that there is a superposition of several effects.

VI. Summary.

The gas pressure phenomena in the alternating and direct current corona have been studied. It has been found that there are four of these phenomena in the corona tube: first, there is a pressure difference which appears between the tube and the wire of the order of magnitude of .005 cm. of water; second, a pressure of the order of magnitude of .3 cm. of water which is able to follow variations of one hundred and twenty cycles per second. Third, there is a pressure which develops in about a second and a half. This has been carefully studied by Warner who showed that it was proportional to the current provided that the heating was kept small so that it would not obscure the effect. Fourth, a pressure due to the heating of the gas which is much slower than any mentioned above.

The author desires to express his thanks to Dr. Jakob Kunz for advice and aid throughout the experiments and to Professor A. P. Carman for facilities furnished.

Laboratory of Physics,
University of Illinois,
August, 1920.

ON THE PRESSURE IN THE CORONA DISCHARGE.

By Jakob Kunz.

Synopsis.

Theory of Pressure Effects Due to the Corona Discharge, in Terms of Ionic Mobility.—The characteristic pressure effect is an excess pressure of from 1 to 3 cm. of water inside a tube concentric with the discharge wire. Assuming that the momentum given the ions by the electric field is transferred to the gas, the author shows that the excess pressure is $i/4\pi u$, where i is the current per unit length of wire and u is the mobility. Using this expression, the *positive mobilities in* H_2, N_2, CO_2, O_2 *and* NH_3 *are computed* from the observed pressure differences, and come out respectively 1.51, 0.50, 0.16, 0.23 and 0.31 times 10^{-2} cm./sec. per volt/cm. The first three values are about half those measured by Hess in the wind of ions from radioactive substances, while the value for O_2 is only one eighth, the low value being perhaps due to ozone. The results so far refer to the mean mobility. Assuming that there are two types of ions, the *percentage of heavy ions* comes out about 13 for O_2. The time for the pressure to rise to its limiting value is computed and comes out in rough agreement with the measurements of Fazel; and an explanation is suggested for the form of the pressure curves obtained by Fazel with A.C. discharges.

It has been shown by E. H. Warner[1] that the initial pressure increase in the corona discharge is proportional to the current, that it varies in the different gases from a small value in hydrogen to higher values in nitrogen, ammonia, oxygen and reaches the highest value in carbon dioxide for a given current. A. M. Tyndell[2] has tried to explain the phenomenon in question as a pure heat effect. He has made an experiment moreover in which the central wire was heated and thereupon the potential difference applied. Instead of increasing, the pressure decreased. This phenomenon is apparently connected with the effect observed by J. W. Davis, that in the rectification of alternating currents through the corona discharge in hydrogen, the wire which was red hot, became dark as soon as the corona appeared. In the previous investigation by means of alternating currents and an oscillograph, C. S. Fazel showed that even in this experiment of Davis and Tyndall the pressure at first in a very short time interval increases and then rapidly decreases. So far the following phenomena have been observed:

1. A very small pressure difference, hardly measurable, between the central wire and the outer cylinder.

[1] Physical Review, Vol. 10, p. 483, 1917. See also the corona discharge by E. H. Warner and J. Kunz, University of Illinois Engineering Experiment Station Bulletin No. 114, 1919.

[2] Phil. Mag., Vol. 35, p. 261, 1918.

2. A pressure increase proportional to the current in the D.C. corona, which appears in about 1.5 seconds after the beginning of the corona. This pressure increase may easily amount to 3 cm. of water.
3. With alternating current a varying pressure increase occurs of about .3 cm. of water with a frequency $2n$ when the frequency of the A.C. is equal to n. These pressure fluctuations are superimposed on the effect mentioned before.
4. A pressure decrease which occurs, when direct current or alternating current corona arises from a hot central wire, after an initial pressure increase.
5. A pressure increase due to Joule's heat which can readily be separated from the effect (2).

The principal phenomenon is the pressure increase mentioned under (2) which we shall try to explain by means of the small mobilities of ions which have been measured by Victor F. Hess [1] in the wind of ions emanating from radioactive substances.

The central wire of radius R_1 in the coaxial corona cylinder of radius R_2 has a positive charge and emits in the corona discharge n positive ions per unit length and per unit time. During the time interval dt every positive ion travels through the distance dr with the velocity $v = dr/dt$. Let the electric force at the point r be E, the charge of the ion e, then the increase of the electric impulse during dt is equal to $eEdt$. We assume that this momentum be transmitted to the molecules of the gas so that a pressure difference dp occurs between r and $r + dr$. Since n ions per unit time cross the surface of the cylinder $2\pi r$, then we get: $neEdt = dp2\pi r$. But $ne = i$ which is the corona current per unit length, hence

$$iE\frac{dr}{v} = dp2\pi r.$$

According to the definition of mobility u of the ions, we have

$$v = uE;$$

hence

$$\frac{i}{u}dr = dp2\pi r \tag{2}$$

or

$$\frac{i}{2\pi u}\frac{dr}{r} = dp \tag{3}$$

or

$$\frac{i}{2\pi u}\log\frac{R_2}{R_1} = p_2 - p_1. \tag{4}$$

[1] Sitzungsberichte der Akademie der Wissenschaften von Wien. Math. Abt., 128, Bd. Heft 6, 1919; 129, Bd. Heft 6, 1920.

The pressure difference between the cylinder and the wire is proportional to the current and inversely proportional to the mobility of the ions. If, however, we attach to the corona cylinder an open manometer, we measure the pressure difference between the inner side of the cylinder and the outer pressure $p_2 - p_0$ and not $p_2 - p_1$. We determine the pressure difference $p_2 - p_0$ in the following way:

$$\int_{R_1}^{r} dp = \frac{i}{2\pi u}\int_{R_1}^{r}\frac{dr}{r},$$

$$p - p_1 = \frac{i}{2\pi u}(\log r - \log R_1). \tag{5}$$

The conservation of mass gives the following equation:

$$\int_{R_1}^{R_2} p 2\pi r dr = p_0\pi(R_2^2 - R_1^2). \tag{6}$$

From (5) we substitute p in (6) and carry out the integration.

$$p_1\pi(R_2^2 - R_1^2) - \frac{i}{2u}\log R_1(R_2^2 - R_1^2)$$
$$+ \frac{i}{u}\int_{R_1}^{R_2} r\log r dr = p_0\pi(R_2^2 - R_1^2).$$

or

$$p_1 = p_0 + \frac{i}{2\pi u}\log R_1 - \frac{i}{4\pi u}\left[\frac{R_2^2\log R_2^2 - R_1^2\log R_1^2}{R_2^2 - R_1^2} - 1\right]. \tag{7}$$

We have moreover:

$$\int_{r}^{R_2} dp = \frac{i}{2\pi u}\int_{r}^{R_2}\frac{dr}{r} = \frac{i}{2\pi u}(\log R_2 - \log r) = p_2 - p. \tag{8}$$

We substitute this last p in equation (6) and obtain:

$$p_2 = p_0 + \frac{i}{2\pi u}\log R_2 - \frac{i}{4\pi u}\left[\frac{R_2^2\log R_2^2 - R_1^2\log R_1^2}{R_2^2 - R_1^2} - 1\right]. \tag{9}$$

From (7) and (9) we obtain again equation (4). The pressure difference $p_2 - p_0$ is now given by the expression:

$$p_2 - p_0 = \frac{i}{2\pi u}\left[\log R_2 - \left(\frac{R_2^2\log R_2 - R_1^2\log R_1}{R_2^2 - R_1^2} - \frac{1}{2}\right)\right].$$

In our experiments R_2 and R_1 had the following values:

$$R_2 = 2.25 \text{ cm.}, \quad R_2^2 = 5.05, \quad \log R_2 = 0.81,$$
$$R_1 = .01 \text{ cm.}, \quad R_1^2 = 10^{-4}, \quad \log R_1 = -4.6.$$

Therefore approximately

$$\frac{R_2^2 \log R_2 - R_1^2 \log R_1}{R_2^2 - R_1^2} = \log R_2$$

and

$$p_2 - p_0 = \frac{i}{4\pi u}$$

or

$$u = \frac{i}{4\pi(p_2 - p_0)}. \tag{10}$$

The total current measured in the corona tube of length l was I, hence $i = I/l$ and

$$n = \frac{I}{4\pi l(p_2 - p_0)} = \frac{I}{4\pi l \Delta p}. \tag{11}$$

This pressure increase Δp is assumed to be due entirely to the corona wind and not partly to the heat of Joule. This latter pressure increase, according to the measurement of Warner, is only about 1/2 per cent. of the observed pressure increase in the first second. The necessary small correction is already contained in the values of Δp that are used in the calculation of the mobilities.

We apply formula (11) at first to the straight lines of Fig. 45, page 85 of the bulletin of Warner and Kunz, in order to determine the ratio of the mobilities of the ions in various gases. We choose always the same current $I = 2.10^{-4}$ amp. and obtain the following ratios:

$$\frac{U_{H_2}}{U_{N_2}} = \frac{p_{N_2}}{p_{H_2}} = \frac{1.3}{0.4} = 3.2$$

while Hess gives 3.5.

$$\frac{U_{H_2}}{U_{CO_2}} = \frac{4.2}{0.4} = 10.5;$$

Hess gives 8.3

$$\frac{U_{H_2}}{U_{NH_3}} = \frac{2.2}{.4} = 5.5$$

$$\frac{U_{H_2}}{U_{O_2}} = \frac{3}{.4} = 7.5.$$

These ratios agree in order of magnitude and in their order with those of Hess. The same values can hardly be expected, as impurities, water vapor, dust particles, for instance, of disintegrated metal have a large influence on the mobilities.

We proceed to calculate the mobilities of the ions. From the straight

lines we find for hydrogen the following values:

$$I = 2.10^{-4} \text{ amp.}; \qquad l = 24 \text{ cm.}; \qquad \Delta p_{H_2} = 0.45 \text{ cm. } H_2O$$

$$U_{H_2} = \frac{2.10^{-4}\, 3.10^9}{4\pi \cdot 24 \cdots 45 \cdot 981 \cdot 300} = 1.51\ 10^{-2} \frac{\text{cm.}}{\text{sec.}} : \frac{\text{volt}}{\text{cm.}}.$$

The results are collected in the following table.

Mobilities $\frac{\text{cm.}}{\text{sec.}} : \frac{\text{volt}}{\text{cm.}}$

	Corona.	α articles, Hess.	Point Discharge, Chattock.
U_{H_2}	$1.51 \cdot 10^{-2}$	$3.73 \cdot 10^{-2}$	5.4
U_{N_2}	$.505 \cdot 10^{-2}$	$1.08 \cdot 10^{-2}$	
U_{CO_2}	$.161 \cdot 10^{-2}$	$.45 \cdot 10^{-2}$	.83
U_{O_2}	$.23 \cdot 10^{-2}$	$1.98 \cdot 10^{-2}$	1.3
U_{NH_3}	$.311 \cdot 10^{-2}$		

In most cases the mobilities are only about two times smaller than those determined by Hess; the mobility of oxygen however is 8.6 times smaller than the value obtained by Hess; this may be due to the formation of ozone which accompanies the corona discharge in oxygen. Conspicuous in the corona discharge as well as in the ionization by α particles are the small values of the mobilities compared with those of the point discharge for instance. We may expect other analogies in those forms of discharge which are distinguished by small mobilities of the ions.

We proceed to calculate the fraction of the heavy ions of Langevin. We write the formula (11) in the form:

$$\Delta p = \frac{en}{u} \frac{1}{4\pi},$$

or for one type of ions:

$$\Delta p_s = \frac{e}{4\pi} \frac{n_s}{u_s},$$

$$\Delta P = \Sigma \Delta p_s = \frac{e}{4\pi} \sum_{s=1}^{v} \frac{n_s}{u_s},$$

when there are v types of ions present. If $v = 2$, then

$$\Delta P = \frac{e}{4\pi} \left(\frac{n_1}{u_1} + \frac{n_2}{u_2} \right) \text{ and } i = e(n_1 + n_2).$$

The fraction of heavy ions is then put equal to α so that

$$n_2 = \alpha n,$$
$$n_1 = (1 - \alpha) n$$

and

$$\Delta P = \frac{en}{4\pi}\left(\frac{1-\alpha}{u_1} + \frac{\alpha}{u_2}\right) = \frac{i}{4\pi}\left[\alpha\left(\frac{u_1 - u_2}{u_1 u_2}\right) + \frac{1}{u_1}\right],$$

$$\alpha = \frac{1}{u_1 - u_2}\left[\frac{\Delta P 4\pi}{i} \cdot u_1 u_2 - u_2\right]$$

or in per cent.

$$\alpha = \frac{100 u_2}{u_1 - u_2}\left(\frac{\Delta P 4\pi u_1}{i} - 1\right).$$

For air we have according to Pollock [1]

$$u_1 = 1.3 \text{ (volt)}; \qquad u_2 = .0003 \text{ (volt)}.$$

For electrostatic units of the field we multiply these numbers by 300;

$$i = \frac{I}{l} = \frac{2.10^{-4} \cdot 3.10^{9}}{24},$$

$$\Delta P = 3.981 \frac{\text{dynes}}{\text{cm.}^2} \text{ for oxygen.}$$

With these numbers we obtain $\alpha = 13.4$ per cent.

We shall now approximately determine the time which the pressure increase requires for its development. Let the average velocity of the ions be $v = uE$, then the average time required by the ions to pass through the distance $R_2 - R_1$ will be equal to

$$t = \frac{R_2 - R_1}{\bar{v}} \text{ and } E = \frac{V}{R_2 - R_1},$$

where V is the potential difference between the cylinder and the wire.

$$t = \frac{(R_2 - R_1)^2}{u.V} = \frac{R_2^2}{u.V}.$$

For $R_2 = 2.25$ cm., $u = 5.05 \cdot 10^{-3}$ (volt), $V = 15{,}000$ volts, we obtain $t = .067$ sec. If however we take into account the heavy ions, for which $u = 3 \cdot 10^{-4}$, then we find $t = 1.1$ seconds, while C. S. Fazel found about 1.5 seconds. For the high mobilities $u = 1.3$ (volt) we find for $t = 2.6 \cdot 10^{-4}$ seconds. For the explanation of the large pressure increase we have to assume the formation of heavy ions with very small mobilities. Apparently we can test this conclusion by means of alternating currents. Before doing this, we shall call attention to one or two corrections which have to be made in formula 10. If the ions which arise from the positive wire do not impart their momentum to the gas, they will impart it to the cathode and the gas pressure will not change.

The momentum imparted to the surface $2\pi R_2$ of the cylinder per unit time will be equal to

$$u_{R_2}E_{R_2}mn = (uE)_{R_2}\frac{m}{e}ne = (uE)_{R_2}\frac{m}{e}i = \Delta p_i 2\pi R_2.$$

In general only a fraction of the ions will transmit their momentum directly to the electrode, *i.e.*, to the outer cylinder, so that the pressure increase observed corresponds only to a certain fraction of the current; in formula (10) we have to diminish the current or to add to the pressure Δp a small positive correction Δp_i. We would have: $i/4\pi u = \Delta p + \Delta p_i$. In the manometer we observe only Δp. If the current $i = 0$, then $\Delta p = -\Delta p_i$; this seems to occur in the case of hydrogen according to Fig. 45 on page 85 of the bulletin. If on the other hand the gas molecules are reflected from the cylinder, then the gas pressure on an external surface element will be increased and we shall have a correction Δp_r in the form:

$$\frac{i}{4\pi u} = \Delta p - \Delta p_r.$$

If now $i = 0$, then $\Delta p = \Delta p_r$; a trace of this may occur in the straight lines of NH_3, O_2 and CO_2 in Fig. 45, where the straight lines meet the axis of ordinates a little above the origin. This effect of course could not be a stationary one.

From the explanation of the principal phenomenon it follows, that if we push the glass tube of the manometer from the cylinder more and more toward the wire, the pressure difference $p_2 - p_0$ can not change, provided that in that point the discharge does not change. If with this method nevertheless very small pressure differences have been observed for the two limiting positions of the gas tube, they can only be reduced to small secondary changes in the discharge. There exists indeed a pressure difference $p_1 - p_2$ which we have calculated, but it cannot be measured with the manometric method here indicated.

The straight lines which express the relation between the current and the pressure increase $p_2 - p_0$, have only been obtained for the positive corona, in which the wire is positive. If the wire is charged negatively, we observe also a pressure increase, which however is subject to strong fluctuations, so that regular observations cannot be repeated. This is apparently due to the character of the negative discharge, which does not spread out evenly over the wire, but consists of beautiful little beads, which are partly stationary, partly travel along the wire. For very short time intervals, however, immediately after the potential difference has been applied, the negative corona appears in the form of a fine uni-

form cylinder of light, which covers the whole wire. During this interval the negative corona pressure is probably stable.

If now we produce the corona with alternating current of frequency n, then during every positive and negative half wave the light ions will travel through the whole layer of gas from the wire to the cylinder, producing a partial pressure increase with a frequency $2n$. This phenomenon has been observed by C. S. Fazel.

If the wire is positive, large positive ions of small mobility will be formed, to which corresponds a large pressure increase dp according to the equation $i/u\ dr = dp2\pi r$. These ions, however, will not reach the cylinder during the first positive half wave of the A.C. The corresponding pressure increase will not reach the manometer; if now the negative wave of the A.C. acts, the large ions may be neutralized or even become negative, they will stand still or travel a little further; if afterwards the wire becomes positive again, the quick positive ions will also charge positively those previously formed large ions, which will travel a little further toward the cylinder, which they will reach only after a certain number of cycles. Thus the resultant pressure increase will be equal to that of a corresponding direct current; upon this positive pressure increase are superimposed small regular fluctuations with frequency $2n$. This phenomenon also has been observed by C. S. Fazel.

It has been shown that the characteristic pressure increase in the corona discharge is due to the fact that the ions impart their momentum to the gas. The pressure increase is exactly proportional to the current. The mobilities are of the same order of magnitude as those determined by Hess. If we assume only ordinary ions and heavy Langevin ions, we find that the latter amount to about 13 per cent. of the total ionization. Of course it is possible that ions of widely different mobilities are formed as those studied by O. Blackwood [1] and P. J. Nolan.[2] The mobilities of the ions formed in the corona discharge will be measured by an independent method. The average time required for the formation of the pressure increase has been calculated. The pressure increase observed by C. S. Fazel with alternating currents has been explained.

I am glad to thank Dr. K. F. Herzfeld of the Institute for Theoretical Physics of the University of Munich for many valuable suggestions.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS,
October, 1921.

[1] PHYSICAL REVIEW, Vol. XVI., p. 85, 1920.

[2] PHYSICAL REVIEW, Vol. XVIII., p. 185, 1921.

BEHAVIOR OF FREE ELECTRONS TOWARD GAS MOLECULES.

By H. B. Wahlin.

Synopsis.

Formation of Negative Ions in Gases.—The theories advanced to account for the appearance of abnormal negative mobilities at low pressures are two: it is assumed that in order to form an ion an electron must either have more than a certain amount of energy (Wellisch) or must have made, on the average, n impacts (J. J. Thomson). To test the Wellisch theory, *the effects of increasing the energy of the electrons* was determined. The fact that the number of ions was not increased is taken to favor the Thomson theory. Assuming this theory correct the *Thomson constant n was determined for* CO, NH_3, C_2H_4, C_2H_2, C_2H_6, C_2H_5Cl *and* Cl_2, using carefully purified gases under varying conditions of pressure and frequency of alternating potential. The results depend on the values assumed for the mobility of the electron in the various gases, but they indicate that for gases in the order given, n decreases progressively from about 10^8 for CO to 10^3 or less for Cl_2.

Conclusions.—CO behaves like N_2; electronegative gases attach electrons more readily than do electropositive gases; the degree of saturation of hydrocarbons does not make much difference.

Mobility of negative ions in chlorine, ethane and ethylene was found by the Rutherford A.C. method to be, respectively, 0.73, 1.30 and 0.91 cm./sec./volt/cm. at atmospheric pressure.

Introduction.

In order to account for the fact that the mobility of the negative ion in a gas ceases to be inversely proportional to the pressure as the pressure decreases, Sir J. J. Thomson[1] developed a theory in which he assumes that the electron has to make, on the average, a number of impacts, n, with the molecules of a gas before uniting to form an ion. If this is the case, it is clear that an electron under the action of an applied electric field will travel a greater and greater distance in the direction of the field as the pressure decreases, before combining with the molecules of the gas. Then, since the velocity of drift of the electron in unit field is great compared with that of the ion, we would expect that the mobility as measured by any of the standard methods would be abnormally high. On his assumption, Thomson has shown that out of q_0 electrons starting from a given plane in a gas the number q that travel a distance x without uniting with the molecules of the gas is given by

$$q = q_0 e^{-\frac{wx}{nk'\lambda \frac{v}{d}}}, \tag{1}$$

[1] Thomson, J. J., Phil. Mag. Sept., 1915.

where w is the mean velocity of agitation of the electrons, k' their mobility, λ the mean free path and v/d the applied potential gradient. In this form the equation is applicable to the Langevin method of measuring mobilities.

Loeb [1] modified this expression so as to make it applicable to the Rutherford method of determining mobilities, when a square wave alternating potential is used, and obtained as an expression for the current, I, to the electrometer

$$I = I_0 e \frac{-w}{nk'\lambda}\left[\frac{d^2(P/760)^2}{V} - \frac{KP/760}{N}\right], \tag{2}$$

where I_0 is the value of the saturation current corresponding to a voltage V, K' and λ are the mobility and the mean free path of the electron at a pressure of 760 mm., K the mobility of the ion at this pressure, p the pressure of the gas, d the distance between the plates and $1/N$ the time for a half cycle of the alternating potential. On the basis of this equation, Loeb determined the values of n for N_2, H_2, O_2, and air, assuming the mobility of the electron to be 200 cm./sec./volt/cm.

A further substitution may be made if the Townsend expression for the mobility of the electron,

$$300K' = \frac{.815e\lambda}{mw},$$

is accepted as valid. Equation (2) then becomes

$$I = I_0 e \frac{-.815e}{300nm(K')^2}\left[\frac{d^2(P/760)^2}{V} - \frac{KP/760}{N}\right]. \tag{3}$$

This expression leaves K' as the only quantity about which there is any great degree of uncertainty. The value of K' for nitrogen has been determined by Loeb recently and has been found to be 2,800 cm./sec./-volt/cm., at a pressure of 75 mm. of mercury and in a field of 20 volts. Just what the values of K' will be in other gases, we cannot at present say, and until these values have been determined, we must make an assumption which probably only approximates the truth. This assumption is that the mobility of the free electron in a gas varies from gas to gas in the same manner as does the mobility of the negative ion. Equation (3) then becomes, when we substitute the known values for e and m,

$$I = I_0 e \frac{-1.9 \times 10^8}{n}(K_{n/K})^2\left[\frac{d^2(P/760)^2}{V} - \frac{KP/760}{N}\right], \tag{4}$$

where K_n is the mobility of the negative ion in nitrogen.

[1] Loeb, L. B., PHYS. REV., Feb., 1921.

From this equation n may be calculated from an experimental current-voltage curve. This is done by substituting the quantities for a point on the curve in equation (4). Owing to the assumptions made in deducing this equation, it is necessary to choose a point near the asymptotic foot of the curve. The value of n thus calculated is very nearly a constant, for varying frequencies of the alternating potential and varying pressures, and in the gases studied by Loeb appears to be characteristic of the gas used. The writer will, in the following pages, present evidence which will assist in showing in how far this is the case and to what extent some of the factors which might influence the attachment of electrons effect the value of n.

Factors Influencing the Attachment of Electrons.

There are three factors which might influence the attachment of electrons in gases:

First, an abnormal condition of the gas such as the presence of an activated form or a particular state of the molecules as regards the electronic arrangement in the outer structure. It is well known that when α-particles or ultra-violet light passes through some gases, changes take place. For example, in oxygen we have ozone (O_3) formed and it is possible that this might attach the electrons more readily than do the O_2 molecules. Now, in general, the amount of activation when ultra-violet light is used to produce the electrons would be comparatively small, but if an electron attaches at every impact with these activated molecules, the effect of a small amount of the impurity would be to change the result greatly. However, in some of the determinations made, the writer varied the intensity of the ultraviolet light by a factor of four with no noticeable change in the readiness with which the electrons attach. Where α-particles are used as a source of ionization, it is possible that enough complete chemical change would be produced to influence the value of n for a gas very markedly.

The second possibility is that the electrons must strike the molecules in a certain place in order to attach.

The third factor that might influence the attachments is the relative energy of the electron and molecule at impact. For in the light of our present knowledge of atomic structure, it is conceivable that the electron must have a certain critical energy of approach in order to combine with the molecule. The question which we must decide, then, is whether or not the mean energy of thermal agitation is sufficient to cause attachments and whether or not an increase of the energy of the electrons above that of agitation will influence the constant of attachment, n. This

question can be answered experimentally as the following considerations will show.

THE EFFECT OF ENERGY ON THE ATTACHMENT OF ELECTRONS.

Wellisch,[3] using the Franck modifications of the Rutherford method for measuring mobilities, found below a pressure of 8 cm. in air, evidence for two types of carriers of negative electricity. One type showed the normal variation of mobility with pressure. The other gave abnormally high mobilities with decreasing pressures. Carriers of this second type, Wellisch considered to be free electrons, and he accordingly concluded that the negative carriers in a gas consist of normal ions and permanently free electrons. To account for these free electrons, he assumed that the energy of the electron at impact must exceed a certain value in order to combine to form an ion. To account for the two kinds of carriers observed, the energy would have to exceed the mean energy of thermal agitation, and Wellisch assumed that this additional energy required comes from the energy of emission of the electrons. In short, the explanation he offered was that in order to make an attachment, the electron must strike another molecule within a certain distance of the parent molecule; *i.e.*, before its kinetic energy of emission has decreased below the critical value necessary to form an ion.

If this explanation is to hold, we should expect that in the Wellisch experiment, there would be no change in the nature of the mobility curves obtained with increasing values of the field driving the electrons through the gauze, until the velocity acquired in the field became comparable with the velocity of emission of the electrons from the molecules under the influence of α-rays. For a small change in the field would not materially alter the chance an electron has of striking a molecule within a certain distance of the molecule from which it comes, the velocity of emission being great compared with the velocity acquired in the field. That the curves actually do change their form for relatively small changes in the field was shown by Loeb,[2] who found that as the auxiliary field is increased, the evidence for the two types of carriers disappeared entirely. This indicates weakness in the Wellisch theory.

A further test of this theory may be made by increasing the energy of the electrons in the auxiliary field to a higher value than was used in the experiments by Loeb, for it is to be expected on the basis of the Wellisch theory that before the electron gains ionizing energy in the field, the number of free electrons passing through the gauze would fall to zero, because the energy acquired by the electrons between impacts would

[3] Wellisch, E. M., Am. Journal of Science, 4, 39, p. 583, 1915. Am. Journal of Science, 4, 44, p. 1, 1917.

then exceed the energy of emission from the molecules when the gas is ionized by α-particles. The electrons would therefore be making impacts with the molecules equal to or exceeding the energy necessary for attachment.

In order to determine whether this is the case, the writer converted the apparatus as used by Loeb in his determination of n, to one of the Wellisch type, the only difference being that whereas Wellisch used a radioactive substance to produce his ionization, the writer obtained his photoelectrically, by letting ultra-violet light strike a speculum metal plate. Fig. 1 (*a*) is a plate of speculum metal; (*b*) is a battery which

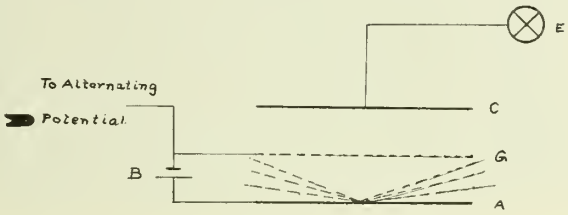

Fig. 1.

produces the field for driving the electrons and ions through the gauze (*g*). (*c*) is a collecting plate 10 cm. in diameter connected to the electrometer (*e*). The alternating potential is connected to the gauze. The distance from (*a*) to (*g*) was made 1.5 cm. and the distance from (*g*) to (*c*) 1.3 cm. The gauze was made by boring holes 1 mm. in diameter in a sheet of brass one half mm. in thickness, the distance between adjacent holes being about 1 mm. With this gauze the writer encountered no difficulty due to the stray field carrying a charge to the collecting plate. Tests were made for a stray field by varying the distance between the collecting plate and the gauze. The current corresponding to a given value of the alternating potential was measured by noting the charge acquired by the collecting plate in a given time. In all this work air was used at pressures of 8 cm. and below. With pressures of from 4 to 8 cm., and with values of the auxiliary field of from 3 to 15 volts/cm., the two types of carriers noted by Wellisch were observed.

As is shown in Curve I. (Fig. 2*A*), with an auxiliary field of 9 volts and at a pressure of 4 cm., the two types of carriers observed by Wellisch are present. With an auxiliary field of 150 volts (II., Fig. 2*A*), the evidence for the two kinds disappears entirely. If the carriers were the normal ions only, this curve as well as III. and IV. in Fig. 2*B*, which were obtained with auxiliary field of 640 and 1,400 volts respectively, should strike the voltage axis at about 35 volts. The curves do change

their form in that the current corresponding to a given voltage decreases for high values of the auxiliary fields. This, however, cannot be taken as evidence for an increase in the number of ionic carriers, as the saturation currents taken with a steady potential showed this same tendency.

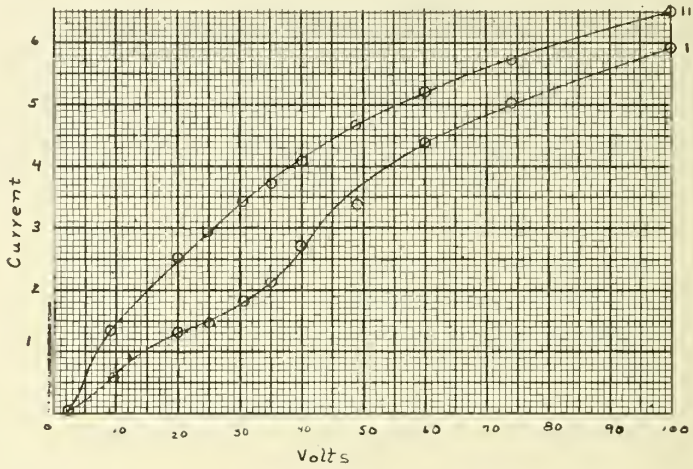

Fig. 2A.

Pressure 4 cm. Frequency of alternating potential, 710 alternations per sec. I.—auxiliary field—9 volts. II.—auxiliary field—150 volts.

We see from these results that an increase in the energy of the electrons above that of thermal agitation does not appreciably influence the number of attachments, and must conclude that the mean energy of agitation at ordinary temperatures is sufficient to cause the electrons to combine with the molecules. This makes the Wellisch theory untenable and leaves as the only alternative which we at present have, the Thomson theory.

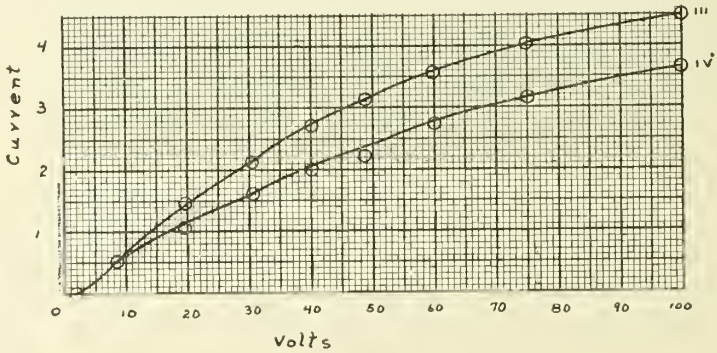

Fig. 2B.

Pressure 4 cm. Frequency of alternating potential 710 alternations per sec. III.—auxiliary field of 640 volts. IV.—auxiliary field of 1,400 volts.

It next becomes of interest to determine the constant, n, of the Thomson theory to see how it varies in different gases with the chemical nature of the gases and with the different types of chemical bonds between the atoms of the molecules of which the gas is composed. Results of this kind may furnish data that will help us to a better understanding of outer atomic and molecular structure.

Determination of the Thomson Constant.

In general, the method used in the determination and calculation of n was the same as that used by Loeb in his experiments. The writer has found the value of n for seven gases; viz., CO, NH_3, C_2H_2, C_2H_4, C_2H_6, Cl_2 and C_2H_5Cl. The determinations were made on at least five different samples of each of the gases, and a number of mobility curves under varying conditions of pressure and frequency of the alternating potential were obtained from each sample. In most cases the pressure variation ranged from 7.6 cm. to 76 cm. and the frequency from 145 alternations/sec. to 712 alternations/sec. Whenever possible, the mobility of the negative sion was determined, and if this could not be done, the values found by other observers were used. In making a series of determinations, the chamber was washed out four or five times with the gas being used, by filling to atmospheric pressure, exhausting to a pressure of 1.5 cm., and filling again. Thus the residual gas from any previous determinations was very small. The value of n was calculated from ten to twelve of the most representative curves for each gas.

In the preparation of the gases, considerable care was taken to get them pure. The importance of this is shown in the work on hydrogen by Loeb. He obtained electronic mobilities in this gas at atmospheric pressure, where other observers had been able to get comparatively low mobilities only. Furthermore, the method of preparation chosen for each gas was such that any impurity present would cause only an unappreciable number of attachments, for obviously the presence of a small percentage of an impurity which attaches electrons readily would change the value of n far more than one which does not. The method of preparation and purification of each gas follows:

Preparation and Purification of Gases.

Carbon monoxide was prepared by the action of concentrated sulphuric acid on sodium formate. The gas evolved was bubbled through a solution of sodium hydroxide in a tower packed loosely with glass wool, which served to break up the bubbles and retard their progress through the solution. The gas was then passed over calcium chloride to remove

any excess of water vapor and over hot copper to break up any organic impurity and remove free oxygen. If there were a trace of oxygen present, there would be some carbon dioxide formed at this point, and in order to remove this, the gas was passed over solid sodium hydroxide. It was then passed over calcium chloride and phosphorous pentoxide to complete the drying, through two traps cooled to liquid air temperatures and finally into the chamber. The cooling served to remove the last trace of any of the more easily condensible impurities. Density tests on the gas checked with the true value to within one part in two thousand.

Ammonia was prepared by heating a solution of ammonium chloride and sodium hydroxide to boiling. A reflux condenser connected to the generating flask removed the excess of water vapor. From this the gas passed over calcium oxide to remove any water remaining and was next liquified in a trap cooled to $-112°$ with frozen alcohol. The liquid ammonia was boiled under reduced pressure to remove oxygen and any of the more volatile impurities, and the liquid thus purified was allowed to vaporize into the chamber first passing through a trap cooled to $-26°$ to remove vapors of stopcock greases.

Acetylene was prepared by the action of water on calcium carbide. The gas was first passed through a series of wash bottles containing solutions of cupric sulphate made slightly acid with sulphuric acid. This removed hydrogen sulphide and phosphine, which are the chief impurities present in acetylene prepared from the commercial carbide. The gas then passed over calcium chloride for a preliminary drying, through a trap cooled to $-26°$ with frozen carbon tetrachloride and was condensed in a second trap cooled with frozen alcohol. About one third of the condensed acetylene was evaporated under reduced pressure. The next third was passed over calcium chloride and phosphorous pentoxide, through a trap cooled to $-26°$, and into the chamber. The remaining third of the gas escaped to the air directly. By this method of fractionation, the less volatile as well as the more volatile impurities would be removed.

Ethylene was prepared by the common laboratory method; *i.e.*, by heating a mixture of concentrated sulphuric acid and ethyl alcohol to a temperature of 165°. The gas evolved was passed through water to remove any alcohol that would be carried over, and through solutions of sodium hydroxide to remove any sulphur dioxide and sulphur trioxide fumes. The water and sodium hydroxide solutions would also remove the greater part of the ether that is evolved in the process. Next the ethylene passed over calcium chloride, then through a trap cooled to $-85°$ with frozen methyl alcohol, and was condensed in a second trap

cooled to $-112°$ with frozen ethyl alcohol. The gas was fractionated and dried by the same method used for acetylene, and then passed through a trap cooled to $-85°$ into the chamber.

Ethane[1] was prepared by the electrolysis of a concentrated solution of sodium acetate in water, the solution being made slightly acid with acetic acid. In the process, hydrogen is given off at the cathode and a mixture of ethane and carbon dioxide at the anode. Care was taken to keep the solution cool during the electrolysis as the efficiency of the process decreases very much with an increase in temperature. Some acetic aldehyde is formed due to the reducing action of the hydrogen, but this, together with the carbon dioxide liberated, was removed by passing the gas through a number of solutions of sodium hydroxide. The process of drying and fractionating was the same as that used for acetylene. Before entering the chamber the gas passed through a trap cooled to $-28°$.

Ethyl chloride was obtained in a pure state from the tubes used by the medical profession for freezing purposes, but was passed through a dilute solution of sodium hydroxide to remove hydrochloric acid gas and then through a solution of sodium thiosulphate to remove any free chlorine that might be present. It was then condensed in a trap cooled to 0°. The process of fractionation and drying was the same as that used for acetylene.

Chlorine was obtained from a tank kindly furnished by Dr. G. L. Wendt, of the Department of Chemistry. During the first two fillings the gas was condensed and fractionated and then dried by passing it over phosphorus pentoxide before it entered the chamber. It was found advisable, however, to dispense with the fractionation, since the gas reacted so rapidly with the metallic surfaces of the chamber that it was necessary to make a filling and take the data in as short a time as possible.

Determination of n for Air and Chlorine.

The writer was unable to get any appreciable photoelectric emission in the presence of chlorine. Although a number of metallic surfaces of different materials were tried, in no case was the emission great enough to be of any use in this experiment. The apparatus was, therefore, converted into one of the Wellisch type, and the ionization was produced by α-particles from polonium. The polonium was deposited on a copper plate which was fastened to the lower side of the gauze (g),

[1] This method is preferable for this experiment to the accepted one for preparing pure ethane; viz., by the action of a zinc-coppered couple on an alcoholic solution of ethyl iodide, since the presence of a trace of any of the halogens as an impurity would alter the results enormously.

(Fig. 1). Care was taken so as to shield the upper part of the chamber from the radiation.

In order that this method shall be applicable to the Thomson theory, the calculations must be made from curves obtained at pressures so low that at least a portion of the electrons liberated pass through the gauze before combining with the molecules of the gas. In other words, the curves must be such as to show the two types of carriers noted by Wellisch. To determine to what extent the method is applicable to the Thomson theory, a series of determinations of n for air was first made. Fig. 3

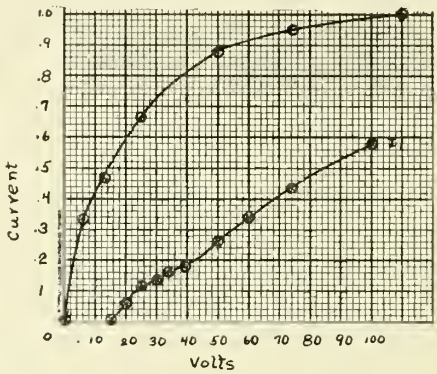

Fig. 3.

Pressure 7.5 cm. Frequency of alternating potential 712 alternations per sec. Auxiliary field—6.0 volts. I.—Mobility curve. II.—Saturation curve. The current is given in fractional parts of the saturation current at 100 volts.

illustrates the type of curve obtained at a pressure of 7.5 cm. The lower part of this curve; *i.e.*, below 42 volts, is due to electrons which get through the gauze before combining. These then start from the gauze as do the photoelectrons in the other determinations of n, and it is therefore from this portion of the curve that our calculations must be made. In this case, the value of I_0 cannot be taken as the value of the saturation current corresponding to the voltage in question. For, obviously, the saturation current is made up of two parts—one part of the current being due to the carriers which start from the gauze as ions and the other part being due to those carriers which start from the gauze as electrons. It is this latter part which determines the value of I_0 in equation 4. Since there is no way in which a distinction between the two types can be made in the case of the saturation current, an approximation to the true value was obtained by assuming I_0 to be equal to the value of the mobility current at the voltage in each case where the electronic carriers predominate. In Fig. 3 this would correspond to the value at 42 volts. However, since the calculations must be made from the lower parts of

the mobility curves, it is necessary to correct this value further for the change in the saturation current as the voltage decreases. So that the value of I_0 thus obtained must be multiplied by the ratio of the saturation current at the voltage in question to the value of the saturation current at the voltage at which I_0 is chosen. In general, a determination thus made would give too low a value for the saturation current, but since in the determination of n, only the logarithm of I/I_0 enters, the error would not be enough to change the results by an appreciable factor. The value of n thus calculated was found to be 4.1×10^4 which compares very favorably with the value of 4.3×10^4 as found by Loeb.

No abnormal mobilities could be obtained in chlorine even at pressures of 1.3 cm. The writer could not work at pressures below this for the ionization produced by the α-particles became so small that the currents were difficult to measure. However, an upper limiting value of n may be calculated if it is assumed that the least ration of I/I_0 that could be measured is .03. Then for the voltage just below the value at which the mobility curve strikes the voltage axis, and for values of the pressure, frequency, and plate distance corresponding to the conditions under which the curve was obtained, a value of n was determined. This will be given in the table below.

Table of Results.

Gas.	n from Equation (4).	K Ionic Mobility.	n from Equation (2).	Limits of Variation of n in Equation (2).	Observer.
N_2	Infinite	2.50	Infinite	——	Loeb
H_2	Infinite	——	Infinite	——	Loeb
CO	1.6×10^8	1.20	3.1×10^7	$(1–6) \times 10^7$	Wahlin
NH_3	9.9×10^7	0.78	1.3×10^7	$(.7–1.6) \times 10^7$	Wahlin
C_2H_4	4.7×10^7	0.91	7.1×10^6	$(.18–1.6) \times 10^7$	Wahlin
C_2H_2	7.8×10^6	1.15	1.5×10^6	$(0.8–2.3) \times 10^6$	Wahlin
C_2H_6	2.5×10^6	1.30	5.3×10^5	$(2.5–8.8) \times 10^5$	Wahlin
CO_2[1]	1.5×10^7	1.22	2.9×10^6	$(2.3–4.3) \times 10^6$	Loeb
CO_2[2]	3.5×10^6	1.22	6.9×10^5	——	Loeb
CO_2[3]	2.1×10^5	1.22	4.0×10^4	——	Loeb
N_2O[4]	6.1×10^5	1.33	1.4×10^6	$(0.8–2.3) \times 10^5$	Loeb
N_2O[5]	3.6×10^5	1.33	7.8×10^4	——	Loeb
C_2H_5Cl	3.7×10^5	0.30	1.8×10^4	$(1.3–2.8) \times 10^4$	Wahlin
Air[6]	4.1×10^4	2.50	1.7×10^4	$(0.7–5.7) \times 10^4$	Wahlin
Air	4.3×10^4	2.50	1.8×10^4	$(0.7–6.4) \times 10^4$	Loeb
O_2	8.7×10^3	2.50	3.6×10^3	$(1.5–5.7) \times 10^3$	Loeb
Cl_2	Less than 2.1×10^3	0.73	Less than 240	——	Wahlin

[1] Freshly prepared.
[2] 4 hours old.
[3] 22 hours old.
[4] Freshly prepared.
[5] 24 hours old.
[6] Using γ-particles.

Results of Determination of n.

The table above gives the values for the mobility of the negative ion used in the calculations of n. It also gives the value of n as calculated from equation 2 and from equation 4, assuming electronic mobility to be proportional to the mobility of the negative ion in both cases.

The values given for the mobility of the negative ion are in most cases higher than the generally accepted values, but the Rutherford method of measuring mobilities gives results which in general are higher than those obtained by other methods. As far as the writer has been able to learn, this is the first time the mobility of the negative ion in ethane, ethylene and chlorine have been determined. Rutherford, however, measured the sum of the mobilities of the positive and negative ions in chlorine and found for this value 2 cm. per sec. per volt per cm. The results on ethane and ethylene were obtained using the Rutherford method and those on chlorine by using the Franck modification of this method.

Discussion of Results.

As will be seen from these results, the values for n calculated on the basis of equation (4) do not agree with those from equation (2), assuming in each case the mobility of the electron to be proportional to that of the ion and independent of the pressure and field strength. Unfortunately our data on electronic mobility are as yet too meager to tell us which set of values most nearly approximates the truth, but whichever set is chosen, the values will serve for comparison of the relative electronic affinites for different gases.

In most cases the value of n is high, showing that the electron does not readily attach itself to a molecule. The fact that in no case is the variation for any gas outside the limits of experimental error indicates that the value of n for a gas is characteristic of that gas. This is further indicated by the fact that the value found for air, using the Franck modification of the Rutherford method and using α-particles as the ionizing source, checks with Loeb's result which he obtained producing the electrons photoelectrically.

It is highly probable that the electron must have a certain critical energy of approach in order to combine to form an ion, but as has been shown, this critical energy is less than the mean energy of thermal agitation, since an increase of the energy of the electrons above that of agitation does not measurably influence the attachments. This leaves two alternatives in explanation of these results; viz., either the electron must strike the molecule in some particular place, or the electron must strike the molecule in some particular state. Whichever explanation holds,

the Thomson theory is still valid, so we have no means of differentiating between the two from the results above.

The fact that n for air is about 5 times the value for O_2 indicates that it is to the O_2 molecule in air that the electron attaches. This would also be indicated by the fact that the N_2 and H_2 molecules do not attach electrons. It is not surprising that these gases give no attachments, for the reluctance the molecules of these gases show for acquiring a negative charge has already been observed by methods of positive ray analysis. J. J. Thomson in his "Positive Rays" states that in no case has a negatively charged nitrogen molecule ever been observed, and only rarely a negatively charged hydrogen molecule.

On account of the resemblance between nitrogen and carbon monoxide as regards a number of their chemical and physical properties, Langmuir[1] and more recently, Thomson[2] have assigned to the molecules of the two gases the same outer molecular structure. Thomson further points out that we should therefore expect a similarity in behavior between the two as regards electronic attachments. As may be seen from the value of n for CO, only rarely does an electron attach to form an ion. In fact, it is possible that it never does. The writer was able to get mobilities for the negative ion in CO of 240 cm./sec. per volt per cm., and although on the Thomson theory this has no significance as a mobility measurement, it will serve to show that the electron will remain free in the gas an appreciable length of time. Such high mobilities have never been obtained before. In the case of NH_3 it is to be expected that the electron will not attach readily, for the NH_3 molecule tends to attach a positively charged hydrogen ion whenever possible and should therefore not show a high degree of electronic affinity.

The results on acetylene, ethylene, and ethane show that as far as the attachments are concerned, there is very little difference between molecules having a double, triple, or a single bond. In a recent paper on the structure of molecules and chemical combinations, J. J. Thomson states that the attachment of an electron to a molecule having a single bond between the atoms might sufficiently loosen the contacts between the atoms so that the molecules would break up. Unfortunately a determination of the mobility of the ion in a gas furnishes us no means for determining if this is the case, since, as has been shown by Wellisch[3] and Franck,[4] the mobility of carriers of atomic dimensions is independent of the size of the carrier. Although it is possible that in some cases the

[1] Langmuir, Irving, Jour. Am. Chem. Soc., 41, 6, p. 868, 1919.

[2] Thomson, J. J., Phil. Mag., March, 1921.

[3] Wellisch, E. M., Proc. Roy. Soc., 82*A*, 509, 1909.

[4] Franck, 9 Ber. d. Dtsch. Phys. Ges., 11, 397, 1909.

attachment of an electron will cause the molecule to split up into a negatively charged atom and a neutral one, it does not seem possible that in a comparatively inert gas like ethane, in which the bond between the two carbon atoms remains intact in most chemical reactions if not in all, the energy of the electron at impact would be sufficient to cause the molecule to break up into a negatively charged atom and a neutral CH_3 group.

The aging effect observed by Loeb in carbon dioxide is as yet unexplained. He prepared the gas by treating pure marble with hydrochloric acid. The writer made a number of determinations in which the gas was prepared by heating sodium bicarbonate, but was unable to get any aging effect. The value of n in this case was more nearly equal to the lowest value in the table above; *i.e.*, to the value after aging. However, the gas in this instance was purified by fractionation and it is possible that in the process of condensation and evaporation, the effect is lost. Loeb also noticed a slight change in N_2O with time and explained it as being due to a dissociation of the gas into N_2 and O_2.

The comparatively high degree of electronic affinity of O_2 and Cl_2 is not surprising, since it is to be expected that the electronegative elements; *i.e.*, those which tend to gain electrons, should show a greater number of attachments than do the electro-positive elements. Furthermore, chlorine, being the more electro-negative of the two, shows the greater tendency to form a negative ion.

That the degree of electronic affinity is determined by the atoms of the molecule rather than by the bonds between the atoms is indicated by the results on ethyl chloride. For by a comparison of the results on this gas with the results on ethane, we see that the replacement of one of the hydrogen atoms with one of chlorine increases the number of attachments appreciably.

This problem was assigned by Dr. R. A. Millikan and was carried out under the directions of Dr. L. B. Loeb. The author wishes to express his thanks to these gentlemen for suggestions and criticisms throughout the progress of the work.

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NOTE ON THE GRAVITATIONAL ACCELERATION OF BISMUTH.

By Harold H. Potter.

Synopsis.

Gravitational acceleration of bismuth has been determined by the pendulum method and found to be the same as that for brass to at least one part in 50,000. This result contradicts the claim recently made by Brush that the acceleration for Bi is much less than for Zn.

In a recent number of the Physical Review,[1] C. F. Brush claimed to have proved by various methods that the gravitational constant for bismuth was less than that for zinc in the ratio 72 to 100. A simple pendulum of suitable design being already in use in this laboratory, Brush's results were checked by the pendulum method.

The pendulum used consisted of a hollow brass bob accurately cylindrical inside and out, suspended by a steel wire from an agate knife edge. The substance on which the experiment was being made was turned into a cylindrical form and fixed inside the hollow brass bob. The method of procedure closely resembled that adopted by Bessel[2] in his famous pendulum experiments. The period of the "experimental" pendulum was compared with that of a standard invar pendulum. A long series of experiments carried out in collaboration with Prof. O. W. Richardson showed that the period of the experimental pendulum—after all necessary corrections had been applied—did not vary by more than one part in 250,000 when various metals were placed in the hollow brass bob.

On the appearance of Brush's paper a cylinder of bismuth was carefully lathe-turned and placed in the bob of the experimental pendulum. The period of the pendulum was then measured, and after the usual corrections had been applied it was found that the period of the pendulum containing bismuth did not differ from that containing brass by more than one part in 250,000. Thus to the limit of accuracy of the experiment the gravitational acceleration for bismuth is the same as that for brass.

An accuracy of one in 250,000 in period represents an accuracy of

[1] C. F. Brush, Phys. Rev., Aug., 1921, p. 125.

[2] F. W. Bessel, Memoire relatifs à la Physique, V., p. 71.

one in 125,000 in the gravitational acceleration. The bismuth weighed 80 gms. out of a total for the whole pendulum of 220 gms.; hence the experiments described above show that the gravitational acceleration for bismuth is the same as that for brass to at least one part in 50,000.

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THE MEASUREMENT OF THE RESONANCE, RADIATION, AND IONIZATION POTENTIALS OF SEVERAL GASES AND VAPORS.

By Paul Edward Boucher.

Synopsis.

Minimum Resonance, Radiation and Ionization Potentials for Various Gases.—A special vacuum tube was used which embodied a modification of K. T. Compton's variable-area electrode by being so designed that either a gauze or a plate electrode could be slid into the position of the fourth electrode. The resonance potentials were obtained from the difference in voltage between successive peaks of the resonance curves; the ionization potentials from Lenard current-voltage curves corrected as to zero by the resonance curves; the relative importance of radiation and ionization at various voltages from the ratio of the Lenard currents obtained with the plate, to the corresponding currents obtained with the gauze electrode having only one fourth the area. The critical potentials in volts, accurate to about 0.1 volt except for toluene, are as follows:

Gas.	Resonance Potential.	Radiation Predominant.	Ionization Potential.
Hydrogen	10.1	10.1 to 13.6	13.6; 15.6
Nitrogen	8.4	8.4 to 15.8	15.8
Oxygen	8.0	None detected	14.0
Ether ($C_4H_{10}O$)	6.6	8.1 to 10.1	13.6
Benzene (C_6H_6)	6.0	None detected	9.6
Toluene (C_7H_8)	6.2 ± 0.2	" "	8.5 ± 0.5
Xylene (C_8H_{10})	6.5	" "	10.0
Chloroform ($CHCl_3$)	6.5	" "	11.5

The results for the resonance potentials for H_2, N_2 and O_2 agree with those obtained by Foote and Mohler, but the values for the corresponding ionization potentials are about 1 volt higher than theirs. The fact that no radiation was detected in the case of O_2 and of all the vapors except ether is rather remarkable; but it may be due to the method used.

A. Introduction.

A CONSIDERABLE amount of research has been carried out on the radiation and ionization potentials of various gases and vapors. The problem has been attacked in several ways but the results are not

in such good agreement as could be desired. The Bohr theory has been applied only to the hydrogen and helium atoms with much success. As time goes on we may expect extensions of this or other theories to other elements and even to compounds. The development of a satisfactory theory rests upon the accuracy with which the radiation, resonance, and ionization potentials can be determined. In this paper the writer describes methods and gives the results in which the critical potentials of several simple gases and compounds have been measured.

Some preliminary work was carried out, in which several ionization tubes of various designs were constructed and tested. Only the final form of the apparatus will be described here.

B. Apparatus.

The problem of distinguishing between radiation and ionization is one of some difficulty. Davis and Goucher [1] have used a modification of the Lenard method in which they reversed the direction of the retarding field between two of the electrodes. A photoelectric effect due to radiation would give a current the direction of which would depend only on the direction of the retarding field, while a positive ion current due to ionization would be obtained with the retarding field in one particular direction. Other observers using the same method have not obtained consistent results.

K. T. Compton in the Philosophical Magazine for November, 1920, describes a three-electrode tube, having a variable area receiving electrode. This electrode consists of a cylinder closed at one end with a piece of foil and at the other with a piece of fine gauze. Either end could be turned towards the cathode, and thus the area exposed to radiation could be changed and a consequent variation in photoelectric current proportional to the area exposed might be expected. If the effect were one of ionization then a variation in the electrode area would not change the current.

The principle of a variable area electrode was employed, though the design was entirely different from that of Compton's. Fig. 1 will give an idea as to its construction. It was a four-electrode tube, though most of the time it was used as a three-electrode tube, two of the electrodes being connected together. The filament A, the platinum cylinder B, and the gauze C were mounted on the glass stopper T. This large glass stopper was fitted to the main part of the tube by a very fine ground glass joint. A small amount of grease was placed around the lower part of the joint, but several days would elapse before the grease could be

[1] Physical Review, Vol. 10, No. 2, August, 1917, p. 101.

noticed working its way towards the vacuum. During the latter part of the work, the grease was entirely removed and the joint was sealed in with a mixture of beeswax and rosin. The ground joint was 8 cms. from the cathode, so that it did not become appreciably warm. Because of the large size of the opening, the entire assembly of the electrodes, *A*, *B*, and *C*, could be removed at will for alteration or repair.

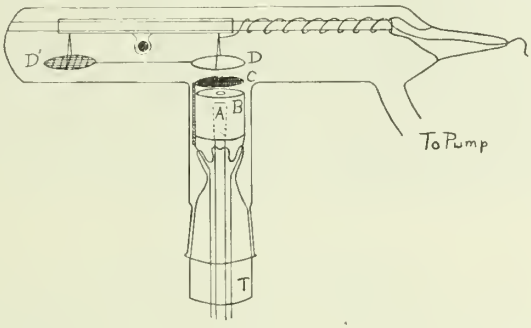

Fig. 1.

The cathode *A* was a piece of platinum foil 1 cm. in length, cut narrow at the center, so that the central portion became much hotter than the ends, thus furnishing the larger portion of the supply of electrons and hence approximating to an equipotential source. It was coated with lime and baryta by giving it several coats of sealing wax and heating it at a high temperature in air before being placed in the tube.

The platinum cylinder was 2 cms. long, 2.5 cms. in diameter, and closed at one end except for a circular opening 0.5 cm. in diameter. The cylinder was thus slipped over the cathode so that the small hole was about 3 mms. directly above the cathode. A fine gauze placed over the small hole was found to improve the operation of the tube.

A small glass stem furnished both the support and the means of insulation for the fine gauze electrode *C*. This electrode was placed 6 mms. distant from the cylinder.

The innovation, the electrode of variable area *DD'*, consisted of a platinum foil disk of 3 cms. diameter, and a very coarse gauze disk of the same diameter. These were connected by a stiff wire 5 cms. long, and the whole was suspended from a glass sleeve. A glass rod fixed permanently in the tube, formed the track upon which the glass sleeve could be moved back and forth. A small piece of soft iron, enclosed in glass, was sealed to the movable electrode at *E*. Thus by means of an electromagnet outside the tube, the electrode could be moved so that either the solid disk or the coarse gauze was directly above the electrode *C*. It was

thought by placing these parts of the electrode 5 cms. apart, that while one disk was directly above C, the other would be too far away to receive any appreciable effect either due to radiation or ionization. The meshes of the coarse gauze were about 6 mms. square. The total effective area of one side that would be exposed to radiation was 7 square cms. for the solid disc, and 1.87 square cms. for the gauze. Thus the ratio of their effective areas was about 3.78. So that if the current received were entirely due to radiation incident on the electrode, it would be almost 4 times larger for the solid disc than for the gauze. A fine coil of platinum wire formed the flexible lead to the outside of the tube. All parts were made of platinum, so that before being connected to the pump, the entire tube was washed several times in nitric acid, rinsed in ammonia and distilled water and then dried in an electric oven.

C. Methods Employed.

Three methods of operation were employed with tube No. 4. Figure 2 shows the connections which were essentially the same for the three methods. The cathode A was heated by four 7-volt Edison storage batteries. This number was found to be advisable in order to obtain steady electron currents, because from 4 to 6 amperes of current were required to raise the cathode to the desired temperature. This source of current was found to be fairly constant. During most of the work, a piece of fine gauze was stretched across the small hole in the cylinder B. In the preliminary tryout of the tube, the cylinder was removed, but the results were very unsatisfactory and it was replaced. C is the fine gauze and DD' is the movable electrode by which the area exposed to radiation could be varied. B and C were connected together most of the time.

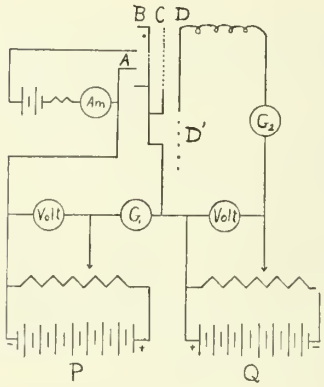

Fig. 2.

The methods employed are called the Lenard, the ratio, and the resonance methods. The Lenard and the ratio methods were used simultaneously, that is, data by which ratio curves were plotted, were obtained from the Lenard readings. Battery P furnished the accelerating potential V_a, which was applied between the cathode and BC. For the Lenard method battery Q furnished the retarding potential V_r, which was applied between the variable area electrode DD' and BC. This potential was always larger than the highest value of the accelerating

potential used, usually about 30 volts. Thus BC was charged plus with respect to A, and electrons from the cathode would move to BC. Some would pass through the gauze covered opening into the space BC, where they would travel at a constant velocity, since the electric field in BC was zero. Those electrons which did not collide with atoms or molecules in BC and possessing sufficient velocity would pass through the fine gauze C into the space CD. Here however the large retarding potential V_r would prevent any electrons reaching D. Let us suppose that the electrons have attained a velocity V_a sufficient for them to cause the atoms they collide with to give off radiation. Then some of this radiation will fall on the movable electrode DD', and due to what is called the photoelectric effect, electrons will be emitted from DD' and due to V_r will pass from DD' to BC, and we will have a current measured by the high sensitivity galvanometer G_2. This special Leeds and Northrup high sensitivity galvanometer had a sensitivity of 5×10^{-11} amperes per mm. deflection. Now the value of the radiation current will depend on the area of the electrode exposed to radiation. Since the ratio of the area of the solid disc to the coarse gauze is about 3.8 we should expect the current to the disc to be almost four times that to the coarse gauze, provided the effect is purely one of radiation. On the other hand if the velocity of the electrons is sufficient to produce ionization by collision, then the positive ions formed will go to the electrode DD', and we will have a current indication on the galvanometer in the same direction as for radiation effects. However if we vary the area of the electrode DD', there will be no change in the value of the current since the ionization does not depend on the area of the electrode exposed. Thus we have a means for distinguishing between radiation and ionization. The procedure in obtaining the necessary data for the ratio test was to take first a reading of the Lenard current with the disc end of the movable electrode above C, then by means of an electromagnet move the gauze end above C, and again read the current value, the accelerating and retarding potentials meanwhile remaining constant. This procedure was continued for each value of accelerating potential applied. Dividing the current value to the disc by the current value to the coarse gauze we obtain the ratios of the currents for the various V_a's applied. And we can conclude, at least with our present knowledge of the subject of photoelectric and ionization effects, that if the ratio approaches 4 in value, the effect is entirely due to radiation; if it becomes 1, then it is due to ionization, while if the ratio has some intermediate value between 1 and 4 both ionization and radiation are present.

The only change necessary to obtain resonance currents is to make the

retarding potential V_r small, say 1 to 5 volts, instead of 30 volts as in the Lenard method. The collisions between electrons and the atoms of some gases appear to be elastic up to a certain velocity. Beyond this point, the collisions become inelastic, that is the colliding electrons give up their energy to the atoms or molecules, which in turn is used to remove one of the atom's electrons from its stable position to an unstable one, and thus radiation of frequency n is produced when the electron falls back into its stable position. Thus when inelastic collisions take place the colliding electrons lose their velocity. If the retarding potential is small and the accelerating potential is increased from zero, the electrons will acquire a velocity which will enable them to reach the electrode DD' against the retarding potential. When inelastic collisions take place, however, some of the electrons lose their velocity and these are unable to reach DD' against the retarding potential and a consequent decrease in electron current takes place. But as the increase in the accelerating potential is continued these electrons again increase in velocity and the electron current begins to increase in value once more. This increase continues, as the potential goes up, until the electrons have acquired a velocity such that inelastic collisions again take place, and we have a second decrease in current. As many as four resonance points in a current voltage curve have been obtained.

It is found that the gas pressure at which resonance curves may be obtained is limited in range. The best resonance curves are obtained between gas pressures of about 0.1 mm. to 2 or 3 mms. No doubt the distance between the electrodes is a factor in obtaining resonance curves, though just how it would affect the critical pressure is not known. The resonance potential may thus be accurately found by taking the difference in accelerating potential between two consecutive resonance points. It should be remembered that an atom or molecule does not necessarily give off radiation at its resonance potential.

The initial correction due to several factors, the initial velocity of the electrons, the contact difference of potential between the cathode and the receiving electrodes, the potential drop along the filament, may be obtained from the resonance curves. In most cases the potential at which the first resonance peak is obtained, is not equal to the difference between two resonance peaks. For any gas the difference between two resonance peaks is found to be always the same no matter what conditions prevailed. The writer found considerable variation in the applied potential difference at which the first resonance peak occurs. Mohler and Foote [1] have published some work on the "Ionization and Resonance

[1] Scientific Papers of the Bureau of Standards, No. 400.

Potentials of some Non-metallic Elements," in which they obtained the first resonance peaks with applied accelerating potentials of smaller value than the resonance potentials as read from the difference of two succeeding resonance peaks. In practically all the work reported in this paper, the initial applied accelerating potentials for the first resonance peaks were either equal to or greater than the resonance potentials. The explanation of this is not clear. It may perhaps be due to contact difference of potential in the cathode itself. We need not know the magnitude of the corrections in order to obtain the proper correction for the Lenard curves. This correction was obtained by taking the difference between the resonance potential and the applied potential at which the first resonance peak begins, and adding or subtracting it as the case may be to the ionization and radiation potentials obtained by the Lenard method.

The general procedure for obtaining the radiation and ionization potentials of any gas was as follows: The tube was first heated to about 300° C. in an electric heater, and the cathode was also heated to a high temperature to help free the electrodes and glass from occluded gas. Liquid air was placed on the trap and the pump was started. This treatment was continued for several hours with a new tube, and was always repeated for an hour or more before each day's work was begun. After such treatment the Gaede pump would give vacuums of the order of 10^{-4} mms. The gas to be tested was then admitted to the desired pressure, and by means of a Geissler tube and an Adam Hilger direct-reading spectroscope, the purity of the gas was tested. If not satisfactory it was pumped out and refilled. Readings were never recorded until the currents became constant in value. After a set of readings was taken, several potentials were rechecked and if the current values varied more than a few mms. deflection on the galvanometer the data were rejected. For any gas pressure data for the resonance curves were first taken and then that for the Lenard and ratio curves.

For admitting the vapors, a bulb connected to a three-way stopcock was sealed on close to the electrode tube. A little of the liquid was poured into the bulb, then it was frozen by liquid air, and all the gas was pumped out above the frozen liquid. The stopcock was then closed, the liquid air removed, and the pure vapor could be admitted as desired. Some difficulty was experienced in admitting the proper amount of vapor. Due to the sudden expansion of the vapor on entering the vacuum, some would condense on the walls of the tube, and considerable time would be required to obtain the desired pressure. It was found however that by first getting a large electron current in vacuum and then just admitting

enough vapor to cause this current to decrease, that the desired pressures could be obtained much more quickly.

D. Experimental Results.

The experimental results obtained in measuring the radiation and ionization potentials of several gases and vapors will now be described in the order performed.

1. *Hydrogen.*

Hydrogen for this test was prepared by the action of caustic potash on aluminum. It was found very convenient to store the gas in a tank under water pressure, so that if any leakage should take place, it would be only loss of hydrogen. A calcium chloride tube was inserted between the storage tank and the ionization apparatus. This tube could be exhausted before admitting hydrogen. The apparatus was always washed out several times with the gas in question before adjusting the

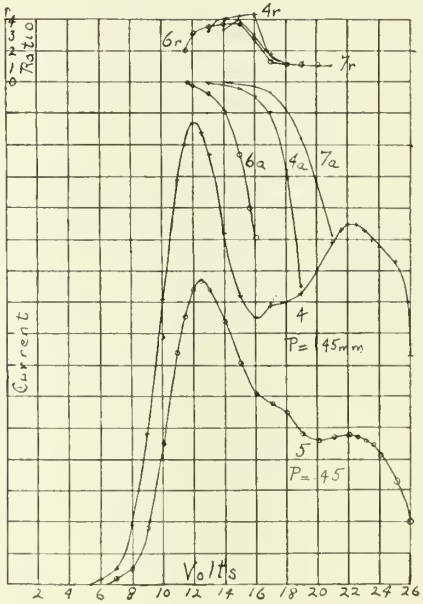

Fig. 3.

pressure for a test. Liquid air was always kept on the trap during these tests. The purity of the gas was tested by examining its spectrum.

Some characteristic curves obtained with hydrogen gas are shown in Fig. 3. Curves 4 and 5 are resonance curves, obtained at the same pressure, but at different filament temperatures. Curves 4*a*, 6*a*, and 7*a*

are Lenard curves obtained at the same pressure but at different filament temperatures. These are the current values measured to the disc of the movable electrode while obtaining the two sets of data from which the corresponding ratio curves were plotted.

The resonance curves give these results:

Curve.	1st Res. Pt.	2d Res. Pt.	Difference.	Correction.
4.....	11.5	21.6	10.1	10.1 − 11.5 = − 1.4
5.....	12.0	22.0	10.0	10.0 − 12.0 = − 2.0

Curve 4 gives a break at 17 volts, and adding the correction (− 1.4 volts) to this gives, 17.0 − 1.4 = 15.6 volts, which is the ionization potential as determined from the resonance curves. Lenard curves 4*a* and 7*a* both have sharp increases in current at 17.0 volts. Referring to the ratio curves this is evidently the potential where strong ionization predominates. Applying the correction we have 17.0 − 1.4 = 15.6 volts for the ionization potential of hydrogen. Curve 6*a* gives a resonance potential at 11.6 − 1.4 = 10.2 volts. Thus it will be seen that the resonance and ionization potentials obtained by the three methods check very well indeed. The break in the resonance curves due to ionization at 15.6 volts was not obtained in all curves. The ionization at this potential evidently prevents the second resonance peak from being as high and sharp as the first. This can be readily explained by the fact that when ionization sets in both plus and minus ions are formed. Remembering that the resonance currents consist simply of electrons possessing sufficient velocity to go against the small retarding potential applied between the movable electrode and *BC*, it will be readily seen that any sudden introduction of positive ions would tend to diminish the electron current, for the positive ions would be attracted by the retarding field to the movable electrode. If the effect were strong enough we might get a complete reversal of current. This has been obtained with some of the vapors worked with and will be referred to again.

The ratio curves deserve further consideration. Radiation and some ionization appear to exist at 10.2 volts. As the accelerating potential is increased the effect becomes principally one of radiation though some ionization is no doubt present. Ionization begins to increase at about 15.0 volts on the ratio curves. Adding the correction (− 1.4) to 15.0 gives 13.6 volts as the potential at which ionization begins to supercede radiation. At this potential the ratio begins to decrease rapidly from 4 until it reaches a value of almost 1.0 at 17.0 − 1.4 = 15.6 volts.

Final Results.

Radiation and some ionization was found at	10.1 ± 0.1 volts.
Radiation predominates between	10.1 to 13.6 volts.
Ionization begins to increase at	13.6 volts.
Strong ionization begins at	15.6 volts.

It is interesting to compare these values with those given by the Bohr theory for hydrogen.

Bohr's theory gives:

Resonance potential	10.16 volts.
Ionization potential of the atom	13.54 volts.
Ionization potential of the molecule	16.26 volts.

There is good agreement between the radiation and resonance potentials, and the first ionization potentials. But the strong ionization found at 15.6 volts does not check quite so well with 16.26 volts as predicted by Bohr's theory. Compton and Olmstead,[1] who first used the ratio method, give 10.8 volts for the resonance potential, 13.4 volts an additional critical velocity, and 15.9 volts the point where intense ionization sets in. The latter two values check fairly well with those found, but there is considerable difference between 10.8 and 10.1 volts.

2. *Nitrogen.*

Nitrogen gas was prepared by heating a solution of ammonium chloride and sodium nitrite in a hot water bath. It was passed through a red hot copper coil and collected against pressure in a storage tank. As before an air tight connection through a calcium chloride tube was used for admitting the gas into the apparatus. Phosphorus pentoxide and liquid air removed the other impurities. The spectrum checked well with that given by Georges Salet in his "Analyse Spectrale."

Some trouble was experienced at first due to what has been called by some writers, polarization effects. Difficulties of this nature have been reported by other observers for various gases. The nature of the trouble seems to be obscure. The character of the resonance and Lenard curves was not affected, but some of the first ratio curves showed that the gauze apparently received more current than the disc. This is difficult to account for, unless the disc was exposed a long time to a freshly coated filament, and some kind of an insulating layer was deposited on it. However this trouble was eliminated by removing the filament base, recoating the filament, and heating all platinum parts to a white heat with a gas flame. The electrodes were replaced and the movable electrode was bombarded by electrons from the hot cathode by applying a potential difference of 50 volts. This trouble was never repeated in the subsequent work.

[1] PHYSICAL REVIEW, Vol. 17, No. 1, Jan., 1921, p. 45.

Fig. 4 shows the type of results obtained. Curve 3 shows three distinct resonance points. In some of the curves four resonance points were obtained. This curve gives a resonance potential between the first two peaks of 8.4 volts. Subtracting from this value the value at which the first resonance point begins, gives an initial correction of − 3.2 volts, which as explained before takes care of all corrections. The Lenard curve 3*a*, at the same pressure (0.4 mms.), gives the first indication of current at 11.5 volts, and a sharp change in slope due to ionization at 19.0 volts. Adding the correction, − 3.2 volts, gives 8.3 volts for the resonance potential and 15.8 volts for the ionization potential.

Fig. 4.

Curve 3*r* shows the ratio of the plate to the gauze current. This ratio is greater than 1 up to 19 volts, where it suddenly drops to a value of 1. It however indicates some ionization as well as radiation before the ionization potential is reached.

Curve 1 shows the arcing potential. It gives a resonance potential of about 8.5 volts and a consequent initial correction of − 3.5 volts. Adding this to the observed potential at which arcing sets in, 20.5 volts, gives the arcing potential as 17.0 volts. The retarding potential used for this curve was only 5 volts, yet here we have an interesting case in which the increase of the accelerating potential from 20.5 to 21.0 volts gives a complete reversal of current, the galvanometer indicating a large positive current instead of an electron current. The magnitude of the

current was too large to measure on the scale. An intense bluish glow was observed when this break in the current curve took place. By using lower pressures and smaller retarding potentials, curves of type 3 were obtained without arcing setting in.

Using the frequency corresponding to the wave-length, = 1492.8 Å., of the isolated doublet in the nitrogen spectrum, observed by Lyman,[1] in the quantum relation, $Ve = h\nu$, we obtain $V = 8.27$ volts. The potential, 8.3 volts, obtained agrees fairly well with this calculated radiation potential. The limiting spectral line corresponding to the ionization potential of nitrogen has not been identified. With the ionization potential of nitrogen equal to 15.8 volts, this limiting spectral line should have a wave-length equal to 782.0 Ångstrom units.

Final Results.

Resonance potential of nitrogen	8.4 ± 0.1 volts.
Radiation predominates between	8.4 and 15.8 volts.
Ionization potential of nitrogen	15.8 volts.

3. *Oxygen.*

An oxone generator was used to generate the oxygen gas, which was said to be 99.4 per cent. pure. It was collected in the storage tank and admitted into the apparatus through a calcium chloride tube. Sometimes the spectrum would show a red line corresponding with that of hydrogen, but this would soon disappear with a hot cathode. Figure 5

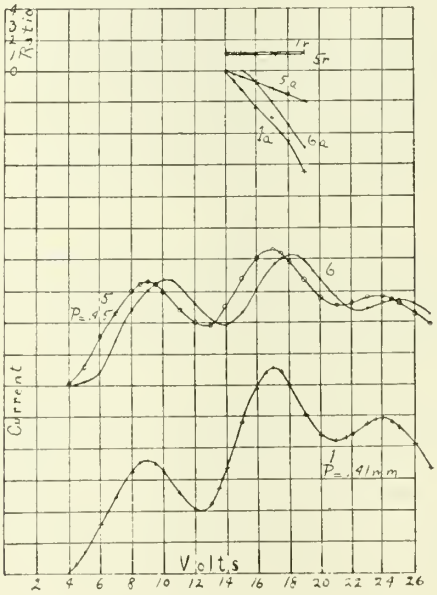

Fig. 5.

[1]Lyman, The Spectroscopy of the Extreme Ultraviolet, p. 113.

shows resonance, Lenard and ratio curves. The best resonance curves were obtained between pressures of 0.5 and 0.1 mm. Three resonance peaks were easily obtained. Curves 1 and 5 give resonance peaks starting at 8, 16, and 24 volts. The true resonance potential is then 8 volts, and there is no initial correction to apply to the corresponding Lenard and ratio curves. Hence the Lenard curves, 1*a* and 5*a*, give the ionization potential as 14.0 volts. It will be noted that no indication of current was found before 14.0 volts. It was sometimes thought that an indication of current could be detected at 13.7 volts, but this is not certain. The increase at 14 volts however was very definite. There is no indication of another ionization potential in the Lenard curves at a higher potential. Mohler and Foote[1] found resonance at 7.9 volts, ionization at 15.5 volts, but no Lenard indication of current before 15.5 volts. The resonance potential checks with that found in this investigation, but there is a difference of 1.5 volts in the ionization potentials. Hughes and Dixon[2] obtained what they called an ionizing potential at 9.2 volts for oxygen. They also state that the curve rises slowly from the axis for several volts, then begins to increase more rapidly. So that it is possible that there is a radiation or ionization effect before 14 volts which is too feeble to be detected in the Lenard method by the galvanometer used. The ratio curves give a value of 1.0 for all accelerating potentials, which means that the current is principally due to ionization from 14 volts on.

Curve 6 was taken immediately after Curve 5. The shift in the position of the curve was caused by reversing the direction of the heating current through the cathode. With Curve 5 the negative end of the accelerating potential was applied to the plus side of the cathode, and reversing the heating current for Curve 6, was the same as applying the accelerating potential to the negative side of the cathode. The resonance peaks of Curve 6 occur at accelerating potentials of about 1.2 volts greater value than those for Curve 5, and this was found to be equal to the potential drop along the filament due to the heating current. Hence we see that the accelerating potentials as read from the voltmeter for Curve 5 are about 0.6 volt less and those for Curve 6 are about 0.6 volt greater than they would have been if there was no potential drop along the filament.

Curve 6 gives 8.0 volts for the resonance potential, and an initial correction of about $8.0 - 9.0 = -1.0$ volt, which added to the corresponding Lenard Curve 6*a*, gives 14.0 volts for the ionization potential, which agrees with the values obtained from the other curves.

[1] Bureau of Standards Publications, No. 400, Oct. 14, 1920.

[2] Physical Review, Vol. 10, No. 5, 1917, p. 502.

Final Results.

Resonance potential of oxygen ..... 8.0 volts.
Radiation was not detected at any potential.
Ionization potential of oxygen ..... 14.0 volts.

4. *Ether* ($C_4H_{10}O$).

Ethyl ether, prepared by Squib for anaesthesia purposes, was poured into the special bulb for admitting the vapors. With the ether frozen by liquid air, the gas above it could be pumped out to a pressure of less than .00075 mm. Then by closing the three way stopcock to the bulb and removing the liquid air, the vapor could be admitted as desired. Pressures between 0.2 and 0.6 mm. gave the best results.

Figure 6 shows some typical curves. Curves 1 and 2 give resonance

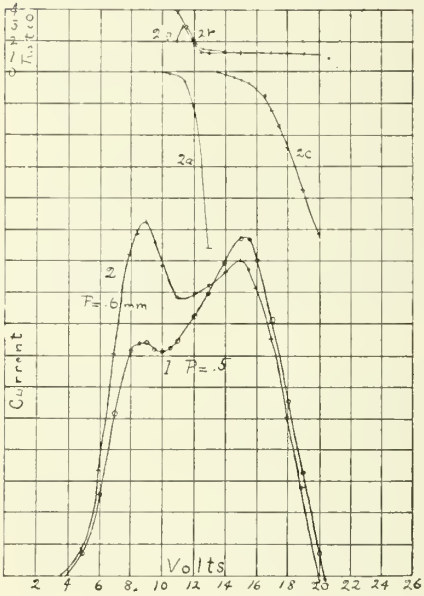

Fig. 6.

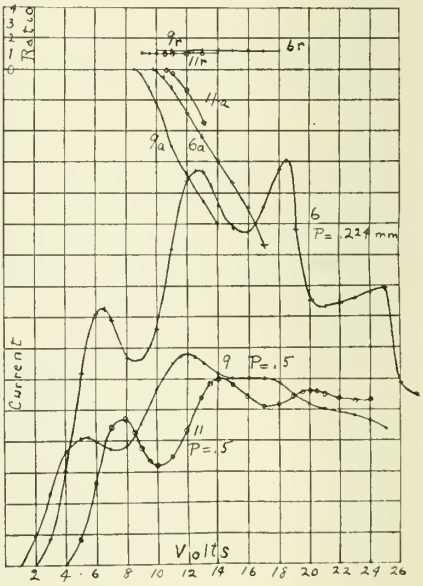

Fig. 7.

potentials of 6.6 and 6.7 volts respectively. The initial correction is − 1.4 volts. Beyond the second resonance point the current decreases rapidly, passes the zero axis and increases in the opposite direction. This effect is supposed to be due to two causes; one a large production of positive ions by ionization by collision, and the other, a decomposition or a chemical action of some kind taking place. It was found that the electron currents were steady in value until the second resonance point was passed. At this point the current would slowly decrease even with a constant accelerating potential, a phenomenon which indicates that some other effect besides ionization by collision is present. It may be

in ether, a compound consisting of carbon, hydrogen, and oxygen, that some kind of decomposition takes place when the molecules collide with electrons having a velocity equivalent to the accelerating potential at which the second resonance peak is produced.

The Lenard Curve *2a* starts at 9.5 volts, and adding the corresponding correction of − 1.4 volts, gives 8.1 volts as the potential at which current is first indicated. Perhaps a more sensitive current measuring device would have indicated a current at the first resonance potential, 6.6 volts. There is a large increase in current at 11.5 − 1.4 = 10.1 volts. Curve *2c* was taken at a lower cathode temperature and it shows a rapid increase at about the second resonance point, 15.0 − 1.4 = 13.6 volts. It is interesting, too, that at large values of accelerating potential, the Lenard currents also decrease with time.

The ratio curves indicate both radiation and ionization up to about 11.5 volts. From here the ratio decreases to a value of 1.0 at 12.5 volts. It is noteworthy that, since oxygen and hydrogen are both constituents of ether, the first indication of the Lenard current, 8.1 volts, agrees with the resonance potential of oxygen, and the increase at 10.1 volts is very close to the resonance potential of hydrogen. Of course additional information will be required before we can determine just what part of the ether molecule is affected when radiation or ionization is produced.

Final Results.

Resonance potential of ether	6.6 ± 0.1 volts.
Radiation and ionization were found at	8.1 volts.
Ionization predominates at	10.1 volts.
Strong ionization was found at	13.6 volts.

5. *Benzene (Benzol)* (C_6H_6).

The benzene used was guaranteed to be of the highest purity and crystallizable by Merck and Co. The benzene vapor gave less trouble than ether. Very little time was required to obtain steady currents.

Fig. 7 gives typical curves for benzene vapor. No difficulty was experienced in obtaining four resonance peaks. It was found that with retarding potentials of 3 volts or more, only two resonance peaks could be obtained, for the electron current beyond the second resonance peak would decrease to zero value and increase in the opposite direction as in the case of ether. The first indications of resonance in Curve 6 are at applied accelerating potentials of 6, 12, 18, and 24 volts, which gives the resonance potential as 6.0 volts with no initial correction to be applied to the corresponding Lenard curves. Curve 9, obtained at a higher vapor pressure, gives first indications of resonance at 5, 11, and 17 volts

and thus a resonance potential of 6.0 volts and an initial correction of $6.0 - 5.0 = + 1.0$ volt.

The corresponding Lenard curves, 6*a* and 9*a*, start at 9.7 and 8.5 volts respectively. Curve 6*a* needs no correction, while Curve 9*a* has an initial correction of + 1.0 volts to be added to 8.5 volts thus making it 9.5 volts. The Lenard curves give no further indication of a critical potential above 9.5 volts. The value of the ratio curves is approximately one at all accelerating potentials, which shows the effect is due principally to ionization.

Before taking the data for Curve 11, the cathode was removed and examined. It was found to be covered with a deposit of carbon, sootlike in appearance. A black deposit of this nature was never noticed while working with hydrogen, nitrogen, or oxygen. Subsequent removals of the cathode while working with xylene have also shown a black deposit. This deposit seems to give a fairly large supply of electrons. The cathode was then recoated with sealing wax and replaced. The curves taken immediately afterwards like Curve 11 required a larger applied initial accelerating potential to produce the first resonance peak than did Curve 9, which was taken at approximately the same gas pressure before the cathode was recoated. So that it would appear that an oxide coated filament requires a larger potential to separate the electrons from it than one with a carbon deposit. Subsequent removals and recoating of the cathode tend to substantiate this statement. Curve 11 gives resonance at 7, 13, and 19 volts and consequently a resonance potential of 6.0 volts, with an initial correction of $6.0 - 7.0 = - 1.0$ volt. The Lenard Curve 11*a* starts at 10.5 volts and adding the correction gives 9.5 volts as the ionization potential.

Final Results.

Resonance potential of benzene	6.0 volts.
Radiation was not detected at any potential.	
Ionization potential of benzene	9.6 ± 0.1 volts.

6. *Xylene* (C_8H_{10}).

Xylene vapor gave similar results to that of benzene. The currents were steady except at accelerating potentials of about 20 volts or more. At these higher potentials both the resonance and the Lenard currents exhibited decreases in value while at a constant accelerating potential. This indicates that some other effect besides ionization is present at these higher potentials.

Fig. 8 gives samples of the curves obtained with xylene vapor. In Curve 5 resonance begins to set in at accelerating potentials of 8.0, 14.5,

and 21.0 volts. This gives 6.5 volts as the resonance potential with an initial correction of − 1.5 volts. Curve 2 shows only two resonance

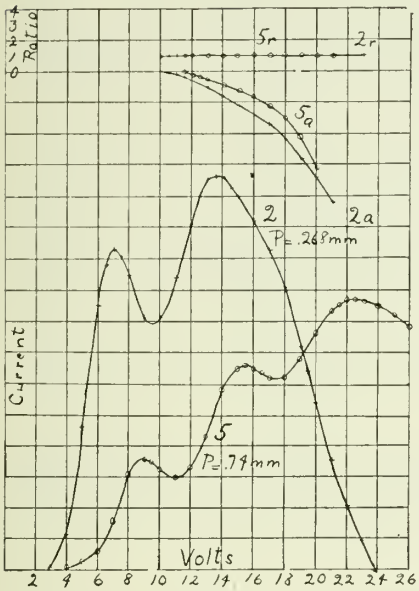

Fig. 8.

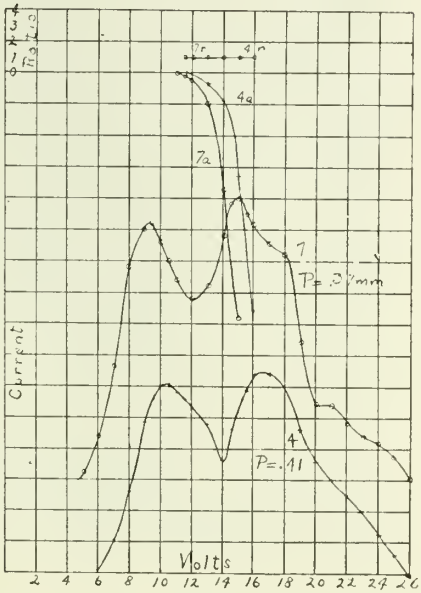

Fig. 9.

peaks beginning at 6.5 and 13.0 volts. The difference gives 6.5 volts as the resonance potential and no initial correction to apply to the corresponding Lenard and ratio curves.

Lenard Curve 5*a* begins at an accelerating potential of 11.5 volts and adding the proper initial correction, − 1.5 volts, gives 10.0 volts as the ionization potential. Curve 2*a* with no initial correction needed, also gives 10.0 volts for the ionization potential.

The ratio curves with a constant value of one, give no indication of radiation at any accelerating potential.

Final Results.

Resonance potential of xylene	6.5 volts.
Radiation was not detected at any potential.	
Ionization potential of xylene	10.0 volts.

7. *Toluene* (C_7H_8).

Some trouble was experienced while working with toluene vapor. The ionization tube had developed a leak, which necessitated the rebuilding of the glass stopper electrode assembly. With vapor present, a large initial accelerating potential of 5 to 6 volts was required to obtain a measurable electron current against a retarding potential of 1 or 2 volts.

The currents were steady until the first resonance peak was passed. Then they were somewhat erratic in their variations at a constant accelerating potential. Sometimes the current deflection would increase a few mms., then decrease a few mms., but always finally coming to rest at a definite position. It was impossible at any vapor pressure to obtain three resonance peaks, though curve 7 gives some indication of a third resonance peak at about 20 volts.

Some characteristic curves of toluene vapor are shown in Fig. 9. Curve 7 indicates resonance setting in at 8.5 and 14.5 volts, which gives a resonance potential of 6.0 volts with an initial correction of -2.5 volts. Curve 4 gives 6.5 volts for the resonance potential with an initial correction of $6.5 - 9.5 = -3.0$ volts.

Lenard Curve 4*a* starts at 11.5 volts and applying the proper correction gives 8.5 volts for the ionization potential. Curve 7*a* also gives $11.0 - 2.5 = 8.5$ volts.

The ratio curves give no indication of radiation. In fact, except for the large initial correction, toluene vapor behaves in a manner similar to that of benzene and xylene. These three belong to the benzene group, and therefore might be expected to give similar results.

Final Results.

Resonance potential of toluene	6.25 ± 0.25 volts.
Radiation was not detected at any potential.	
Ionization potential of toluene	8.5 ± 0.5 volts.

8. *Chloroform* ($CHCl_3$).

Commercially pure chloroform was used during this test. The filament had been freshly coated before admitting the vapor. After working several hours the filament was examined and no traces of carbon deposit could be detected. The electron currents obtained in chloroform vapor were always steady and apparently no decomposition of the vapor took place.

Fig. 10 shows some typical chloroform curves. Curve 2 gives a resonance potential of 6.5 volts with a correction of $+1.0$ volt, and likewise Curve 4 gives a resonance potential of 6.5 volts with a correction of $+1.5$ volts.

The Lenard Curves 2*a* and 4*a* give respectively 10.5 and 10.0 volts, both of which with the proper corrections, give 11.5 volts as the ionizing potential at which the Lenard current is first detected.

The ratio test gave a value of one for all accelerating potentials, showing that radiation was not present in a measurable quantity.

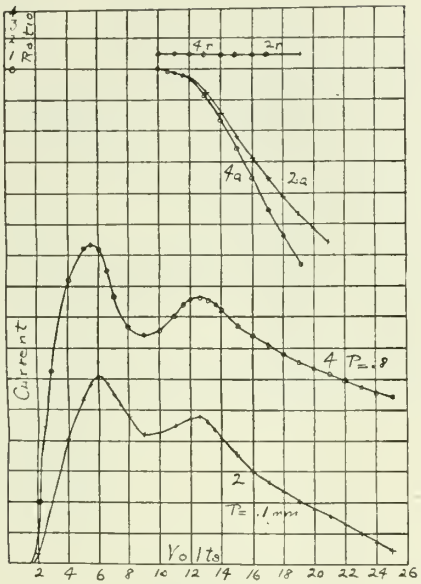

Fig. 10.

Final Results.

Resonance potential of chloroform	6.5 volts.
Radiation was not detected at any potential.	
Ionization potential of chloroform	11.5 volts.

The resonance potentials of hydrogen, nitrogen, and oxygen agree well with those obtained by Foote and Mohler,[1] who used the same method. The ionization potentials of these three gases as found in this investigation using the Lenard method, are respectively about one volt lower than those given by Foote and Mohler. This discrepancy may possibly be attributed to the method of making initial corrections, a difference in galvanometer sensitivity, and the design of the tube.

The indication of radiation in hydrogen as given by the ratio curves agrees well with that given by the ratio curves of Compton and Olmstead.[2] Strong radiation was found to predominate between the resonance and ionization potentials of nitrogen, while no radiation was detected in oxygen.

[1] Scientific Papers of the Bureau of Standards, No. 400.

[2] Physical Review, Vol. 17, No. 1, Jan., 1921, p. 45.

E. CONCLUSION.

Table of Results. (In volts.)

Gas or Vapor.	Resonance Potential.	Radiation Predominates.	Ionization Potential.
Hydrogen—H_2	10.1 ± 0.1	10.1 to 13.6	13.6 15.6
Nitrogen—N_2	8.4 ± 0.1	8.4 to 15.8	15.8
Oxygen—O_2	8.0	No radiation detected.	14.0
Ether—$C_4H_{10}O$	6.6 ± 0.1	8.1 to 10.1	13.6
Benzene—C_6H_6	6.0	No radiation detected.	9.6 ± 0.1
Toluene—C_7H_8	6.2 ± 0.25	No radiation detected.	8.5 ± 0.5
Xylene—C_8H_{10}	6.5	No radiation detected.	10.0
Chloroform—$CHCl_3$	6.5	No radiation detected.	11.5

So far as is known the critical potentials of the vapors used have not been heretofore determined. The resonance potentials for the vapors have about the same values, all lying between 6 and 7 volts. The ionization potentials also occur at a limited range of accelerating potential lying between 8 and 10 volts. Radiation was detected only in the case of ether. If it is present in the other vapors it is too small to be detected by the method used.

It should be noted that the results of this investigation indicate that in many cases inelastic collisions between the electrons and atoms take place without a measurable quantity of radiation being given off. Either this is due to a lack of sensibility in the detecting device, the method of measurement used, or the energy absorbed by the atom from the colliding electron is dissipated in some unknown manner.

Hughes and Dixon [1] found the ionization potentials of acetylene C_2H_2, methane CH_4, ethylene C_2H_4, and ethane C_2H_6, to be between 9.5 and 10.0 volts, which is of the same order as the ionization potentials of the vapors measured in this investigation. So that the hydrocarbons so far measured have approximately the same ionization potential.

The ionization potentials of the compounds are less than those of the simple elements of which they are composed. At least they are less than those of hydrogen and oxygen, the ionization potential of the carbon molecule not being known. This result might be expected from a consideration of the theory of the structure of the molecule. For

[1] PHYSICAL REVIEW, Vol. 10, No. 5, Nov., 1917, p. 495.

instance in a molecule containing a large number of electrons, the repulsive forces of neighboring electrons acting on any one electron will weaken the attractive force between it and the positive nucleus. So that such a molecule could be caused to give up one of its electrons with a smaller input of energy than a molecule containing say, only one or two electrons. No definite conclusions can as yet be drawn as to what part of the molecule is ionized. The loss of an electron by a molecule may mean a rearrangement of the remaining electrons about the nucleus, or it may mean the loss of an electron from one particular atom in the molecule.

In concluding the writer wishes to express his thanks to Dr. H. A. Wilson, under whose direction this investigation was carried out.

The Rice Institute,
Houston, Texas.
May, 1921.

MULTIPLE VALENCY IN THE IONIZATION BY ALPHA RAYS.

By T. R. Wilkins.

Synopsis.

Valency of Ions Produced by α-rays.—The well-known Millikan oil-drop method, in which the valency of individual ions caught on the droplet immediately after they are produced is determined by the change of speed of the droplet due to each, was used with slight modifications which simplified the procedure. *In air*, out of 350 positive ions produced by x-rays at the end of their range, only 3 per cent. could have been doubly charged and most if not all of these were probably not doubles but two successive singles. *In helium*, an extensive series of 2,150 positive catches were observed with gradually increasing pressure to determine not only whether doubles were produced but also the *variation of the number of doubles with the range.* It was found that an appreciable proportion of real doubles is produced when the ranges of the rays are equivalent to between 4 and 30 mm. of helium at atmospheric pressure, the maximum proportion being about 10 per cent., for the range of maximum ionizing power. That this result was real was proved by the fact that when *hydrogen* was substituted, even for the range of maximum ionization, the proportion of apparent doubles was only 5 out of 200 positive ions. The previously reported negative result for *mercury dimethyl* was confirmed.

Relative stopping power for α-rays, of air and helium, came out close to 3.8, in agreement with the Bragg-Kleeman law.

Introduction.

THE nature of the process of the ionization of gases by alpha rays was investigated by Millikan, Gottschalk, and Kelly [1] by catching an ionized molecule upon an oil-drop at the instant of ionization and then measuring the charge thus added to the drop. The results prove that at least 99 times out of 100, ionization by an alpha ray, in the case of the following gases and vapors (air, carbon dioxide, carbon tetrachloride, methyl iodide, and mercury dimethyl), consists in the detachment of a single electron from a molecule.

These results, along with much other work, summarized by Millikan, Gottschalk and Kelly, point to the formation of univalent ions. Indeed the only evidence for the formation of multivalent ions was the positive ray work of Sir J. J. Thomson.[2] Millikan pointed out, however, that these results were not at all irreconcilable, as a consideration of the velocities and the forces involved, made it conceivable that slow positive rays might make multivalent ions when fast alpha rays would not. It

[1] R. A. Millikan, V. H. Gottschalk, M. J. Kelly, Phys. Rev., 15, 157, 1920.

[2] J. J. Thomson, Rays of Positive Electricity and their Application to Chemical Analysis. Longmans, Green & Co.

became desirable, therefore, to test this point and, accordingly, such work has been undertaken.

Reference was also made to the scintillation experiments of Sir Ernest Rutherford on the "swift atoms" resulting from ionizing gases by the nuclear impact of alpha rays, in which the inference was drawn from negative, rather than positive evidence, that doubly charged ions of helium were formed. The importance of extending the oil-drop experiments to include a study of the alpha-ray ionization of helium was obvious, both because of the fundamental rôle played by the helium atom in the present-day theories of atomic structure and the fact that in alpha rays themselves we really have doubly charged helium ions. Recently it has become possible to secure helium in sufficient quantities for use in the oil-drop apparatus, the chamber of which has a volume of about twenty litres, and the results of a study of the alpha-ray ionization of helium are here given.

The results in helium, as will appear, made it seem desirable to extend the work to hydrogen, and this has also been done.

Apparatus.

The apparatus used was identical with that already described [1] except that polonium was used instead of radium bromide as a source of alpha rays. Unfortunately polonium was not available at the time of the earlier work. While not altering the procedure in any way, this substitution brought two advantages: first, it removed the annoyances encountered in the earlier work which were caused by the formation of an "active deposit" on the walls of the chamber, and the consequent increased and uncontrollable ionization due to this cause; secondly, it provided a "simple" source of ionizing rays for which a random distribution of ejection could be assumed in a study of the frequency of catches.

The polonium was prepared by Mr. E. T. Johnson and Mr. B. A. Rogers, who also conducted some observations on the ionization of air, to which reference will be made later. To obtain the polonium some old radium preparation was used and the usual method followed.[2] The product was tested in an electroscope for the presence of beta rays by covering it with sufficient aluminum foil to absorb the alpha rays but not the beta rays, and it was found free of beta radiation.

The coarse adjustment to obtain ionization at the end of the range was made by interposing absorbing foil of the necessary thickness and the finer adjustment made by varying the gas pressure in the chamber. In this way a very delicate adjustment could be obtained.

[1] R. A. Millikan, V. H. Gottschalk, M. J. Kelly, loc. cit.

[2] Practical Measurements in Radioactivity, W. Makower and H. Geiger, Longmans, Green & Co., p. 123.

A concentrated filament lamp replaced the arc used in the earlier work and gave a very steady illumination and did away with the necessity of frequent adjustments of the arc.

A potentiometer switch was arranged so that the plate voltage could be varied through wide ranges in steps of 15 volts.

PROCEDURE.

The general procedure followed was that already described.[1] For the greatest possible simplicity of observation it was always arranged to have but one charge on the drop when the polonium door was open.

The field between the condenser plates was adjusted to balance the drop when it had this one charge on it and measurements were made at this one voltage. Thus the duties of the experimenter were very much lightened. As soon as a catch was made and measured, the drop was made ready for another catching by getting rid of all but one charge. This was done in the usual way.

The experimental testing of the number of charges on the drop is very simple under this procedure for there is then clearly an exact multiple relation between the characteristic speeds corresponding to various numbers of charges. And, further, no time is wasted in first determining the characteristic speeds or in redetermining them as the voltage of the cells drops, for if the voltage drop, the potentiometer switch is moved a peg till the original balance is secured. This was of help in the work on mercury dimethyl vapor, where the temperature was raised considerably to raise the vapor pressure while a run was in progress. No confusion resulted, for although the numerical values of the speeds changed, each one altered so that a multiple relation again held. For example, the speed corresponding to a catch of one charge changed from 16 to 18 seconds as the temperature and vapor pressure rose. That corresponding to a catch of a double rose, proportionately, from 8 to 9 seconds, and similarly, the triple speed changed from 5.3 to 6 seconds.

To express these relations in mathematical form, we have the two following equations:

(1) $V_g = kmg$ where V_g = the vel. of fall under gravity.
k = a constant of proportionality.

(2) $V = k(neE - mg)$ V = vel. of rise when the drop has a positive charge.
n = number of charges on drop.
e = the elementary charge.
E = the P.D. between condenser plates.

[1] Millikan, Kelly and Gottschalk, loc. cit.

Now, if $Ee = mg$, *i.e.*, if the potential applied is just sufficient to balance a drop with unit charge, (2) becomes,

$$V = k(n - 1)mg. \tag{3}$$

and so if

$$n = 1, \quad V = 0.$$
$$n = 2, \quad V = kmg.$$
$$n = 3, \quad V = 2kmg.$$
$$\text{etc.}$$

thus, when a charge is caught, the drop will start upward with a speed equal to kmg—if two charges are caught, with twice that speed; and if three charges are caught, with three times that speed, and we immediately have the number of charges caught because of this multiple relationship in speeds.

As evidence of the careful balancing of the drop and the control of the ionization, it may be mentioned that the drop was often left suspended for intervals of a quarter to half an hour and in one case a drop was left for an hour and a quarter and was in practically the same spot when the observers returned from dinner.

An attempt was made to take as long runs as possible on the same drop and in no case have fewer than 21 catches been reported on the work in air and in the work in helium not fewer than 50 catches of positives. As many as 150 catches are reported on some drops corresponding to from six to eight hours' observation on the same drop. Most of the drops remained bright right up to the end of the run, but in the work on mercury dimethyl vapor, where an attempt was made to raise the vapor pressure by raising the temperature some 15 or 20 deg. C., the drops soon lost their lustre and only short runs were possible.

Data—Air.

Table I.

Drop Number.	Pressure (Cm. of Hg).	t_g (Secs.).	Total No. of Catches (Pos. Negatives).	Double Positives.
1	8	103	95	2
2	8.1	95	21	0
3	8.1	150	68	1
4	8.05	102	35	0
5	8.1	105	108	0
6	8.15	114	66	3
7	8.3	103	21	0
8	8.15	138	48	2
9	8.2	110	52	2
			514	10

Table I. shows that out of 514 catches, 350 of which were positives, 10 were apparently doubles. It will be noted that the work here summarized was all done at approximately the same pressure. About as many more data were first taken under various conditions of pressure to determine the most suitable value at which to work. If the pressure is a little too low, too many alpha particles get through and the catches come too frequently. If the pressure is too high, the interval between catches becomes too long. It was thus found desirable with rays already slowed down by aluminum foil to the extent these were, to work with air at pressures between 8 and 8.5 cms. This corresponded very nearly to the end of the range of the alpha rays.

The column t_g represents the time taken for the drop to fall 50 scale divisions, approximately 5 mm., under gravity and thus indicates, roughly, the smallness of the drops.

In another set of observations of this same kind in air taken by other observers, namely Messrs. Johnson and Rogers, 519 catches of positive ions were made on 18 drops under approximately the same conditions as those just summarized. They found 15 catches which they counted as doubles and 5 which, though measuring up as doubles, they classed as "doubtfuls." By a doubtful double they meant that two jerks were observed in the drop's motion—a second jerk taking place before the shutter could be closed to prevent further ionization. While the second jerk might have been a Brownian movement jerk, as it often proved to be when measurement showed only a "single," yet it was felt that the second jerk might have been caused by the catching of a second ion and such catches were therefore classed as doubtful doubles.

It will be seen that these two sets of measurements are in very good agreement; Johnson and Rogers data showing about one double in 34 positive catches and the data here given showing one in 35.

To decide whether these were real doubles or whether a large fraction of these, too, were actually doubtful doubles, it was only necessary to find what was the average interval during which the polonium shutter was open before a catch was made and to calculate what the chance would be of two single ions being caught in an indistinguishably small interval. The observations showed that if the pressure was 8.1 cms. (in the case of air), the average exposure for a catch was 43 secs. but when the pressure rose, less than half a cm., to 8.5 cms. of mercury, the interval increased to 167 secs. and when a pressure of 9 cm. was reached, no catches were made after several intervals of ten or fifteen minutes, waiting. Hence, for alpha rays which had already been slowed down by the foil to the extent which these had, a pressure of between 8.1 and 8.5 cms.

of air enables us to make measurements at practically the end of the range. The discussion of the probability of two single ions being caught in an indistinguishably small interval is given below.

The Probability Function.

It has been shown repeatedly that a random distribution of ejection can be assumed for the alpha rays emitted in radioactive changes. But it is a familiar result, taken from the theory of probability, that if a series of events happens with a random distribution of intervals, the probability of there being an interval as long as t seconds between two successive events is

$$P = e^{-ut}, \tag{1}$$

where $1/u$ is the average interval.

It was estimated that 1 second was a fair value to take for the time interval within which it was impossible to distinguish with certainty two successive catches as actually separate events for it required about this time for closing the shutter after a catch had been seen to have occurred and during the act of closing another catch might occur without being noticeable. In the various measurements made, the average interval varied from 13 to 170 secs. The probability function may be calculated for each interval but it will be legitimate for the purpose in hand, to consider only the general average, namely, 43 secs.

From (1), the probability of an interval as long as 1 sec. between two successive catches $= e^{-u}$. The probability that there will be an interval between 0 seconds and 1 second $= 1 - e^{-u}$. Now

$$e^{-u} = 1 - u + \frac{u^2}{2!} - \frac{u_3}{3!} + \text{etc.}$$

$$1 - e^{-u} = u - \left(\frac{u^2}{2!} - \frac{u_3}{3!} + \text{etc.}\right)$$

With $u = 1/43$, all terms of the last expression, save the first, are negligible, *i.e.*, the chance of two successive catches following within an interval of 1 sec. is simply u.

It appears then that since the average interval, as given below, is about 43 secs., that one catch in 43 under such conditions should appear as a double. This number is so near the total number of doubles obtained that we are justified in the assertion that no evidence is herewith presented for the formation of doubles in air. We may at least conclude with certainty that the act of ionization of air by alpha rays produces no more than two or three per cent. of doubly charged ions and practically never produces ions of larger valency than 2.

HELIUM.

It was decided to undertake quite an extensive investigation of helium as no work of this type had been done in that gas. Accordingly some 2,150 positive ions were caught; an attempt being made to approach *gradually* to the end of the range of the alpha particles. This was done by gradually increasing the helium pressure in the oil-drop chamber as successive oil drops were blown in with helium. As the "stopping power" of helium is much less than that of air, it was found that to slow down the alpha particles to the end of their range, a much larger helium pressure was required than was necessary in air. The gas pressure was steadily increased and measurements taken at various stages.

DATA—HELIUM.

It will be noticed from Table II. that the interval between catches decreased at first as the pressure was increased since more atoms of helium were present to be ionized. The interval became a minimum

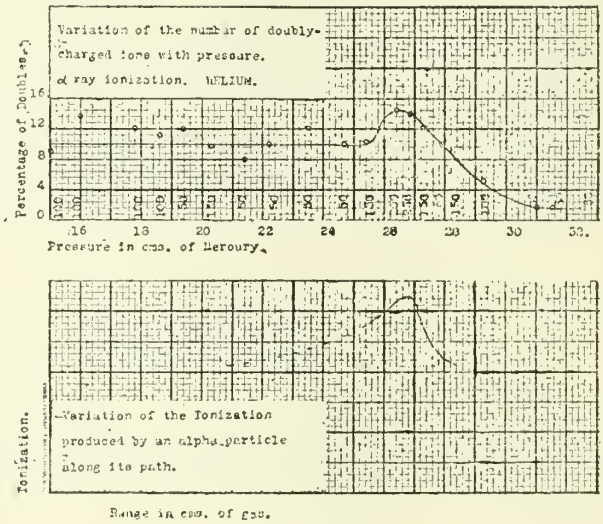

Fig. 1.

at a pressure of about 26.6 cms. and then gradually increased indefinitely. Thus the ionizing power of the alpha ray is a maximum a short distance from the end of its range, which is in agreement with other work. (See Fig. 1.) As the pressure was further increased, the number of alpha rays getting through was cut down and so the interval was lengthened.

TABLE II.

Press.	No. of Positives Caught.	t_g of Drop.	Average Interval.	Per Cent. Doubles.	Average Per Cent. Doubles.	Range Beyond Point of Lip.*
8.9	50	74 secs.	44 secs.	2	2	4.0 cm.
13	50	73	23	4	4	3.3
15	100	112	19	9	9	
16	100	78	18	14	14	2.8
17.8	100	98	17	12	12	2.5
18.6	50	99	18	10	11	2.4
18.7	50	109	13.6	12		
19.4	50	113	20	12	12	2.3
20.1	50	127	21	16	9.3	2.1
20.3	50	108	27	6		
20.3	50	129	23	6		
21.4	50	141	20	8	8	1.9
22.2	50	127	31	10	10	1.8
23.5	50	124	28	12	12	1.6
24.7	50	130	27	10	10	1.4
25.4	100	140	26	9	10.5	1.3
25.5	50	143	26	12		
26.3	50	142	23	14	14.7	1.1
26.4	50	161	29	18		
26.6	100	155	17	12		
26.8	150	163	26	9	14	1.0
26.85	50	192	30	20		
26.9	100	139	23	13		
27.1	50	163	20	18	12	1.0
27.3	50	157	39	2		
27.5	50	174	31	16		
27.9	50	135	40	10	10	0.8
28.1	50	157	30	6	9	
28.4	100	171	28	12		
29	50	153	66	4	5	0.7
29.5	50	154	56	6		
30.95	50	138	67	2	2	0.3
31.5	50	155	88	2	2	
32.5	50	148	154	2	2	0.08
	2150					

The data show distinct evidence for the formation of doubly charged helium ions and show, moreover, that the formation of doubles does indeed depend on the speed of the ionizing particle. The number of doubles rises to a maximum when the ionizing power of the particles is a maximum and amounted, in this work, to as many as 15 per cent. of

* Reduced to atmospheric pressure. This reduction was suggested and outlined by Dr. G. S. Fulcher. It indicates that doubles are produced when the ranges of the rays are equivalent to between 4 and 30 mm. of helium at atmospheric pressure.

the number of ions formed. The probability of two singles being caught in an indistinguishably short interval would not account for more than three or four per cent. of the total catches being doubles, for the average interval at the peak of the production of doubles was about twenty-five seconds and thus, on the basis of the reasoning given above, one ion in twenty-five might be expected to be a spurious double. This still leaves a large margin for considering this a real effect, and this is made even more apparent in the light of some remarks under the head of hydrogen, below.

Grouping the data corresponding to pressures between 15 and 24 cms., it will be seen that the number of doubles is about 10 per cent. of the total number of positive ions produced, but from this region to the end of the range, a marked rise and subsequent decline is noticeable. Large fluctuations appear from this 10 per cent. but this is to be expected from any such probability measurement as this if only a small number of observations is taken. There seemed no special object in multiplying the observations in this region, but there was reason to expect that the region toward the end of the range might prove of special interest, for Geiger had shown, as is checked by the data above, that toward the end of the range the ionization rises very markedly.[1] Accordingly, a much larger number of observations was made in this region, and Fig. 1 shows that the curve is fixed quite definitely for this region of interest.

An interesting comparison may be made between the data on air and those on helium. It was found, as already noted, that with air, an interval of 167 secs. ensued between catches if the pressure were raised to 8.5 cms. Table II. shows that in helium an interval of 154 seconds accompanied a pressure of 32.5 cms. So the alpha particles were ionizing about as infrequently in one case as in the other. In other words, 8.5 cms. of air have about as great stopping power for alpha particles as 32.5 cms. of helium. This is in very nice agreement with Bragg and Kleeman's results that the stopping power of an element for alpha particles is proportional to the square root of the atomic weight and for complex molecules is an additive property.[2] Adams has already done work on the testing of this law for helium and other gases.[3] Using Adams's calculations for

$$\frac{\Sigma\ \sqrt{\text{At. Weight air}}}{\Sigma\ \sqrt{\text{At. Weight helium}}} = 3.8$$

and remembering that the stopping power is inversely proportional to

[1] Rutherford, Radioactive Substances and their Transformations, p. 153.

[2] Bragg and Kleeman, Phil. Mag., 6, 1905, p. 338.

[3] Adams, PHYS. REV., 24, 1907, p. 108.

the pressure, we calculate that the pressure of helium necessary to stop the alpha particles to the same extent as would be done by 8.5 cms. of air would be 8.5 × 3.8, or 32.3 cms. of helium. This is to be compared with the 32.5 cms. for approximately equal stopping power mentioned above.

Hydrogen.

The law given by Bragg and Kleeman for the stopping power of gases for alpha particles has been shown, above, to be beautifully checked in the work on helium. It follows from the law, that hydrogen should have the same stopping power as helium, for though of different atomic weight, helium is monatomic and hydrogen, diatomic. If the doubles in helium were spurious in any way, the same effects should occur in hydrogen. A series of runs was therefore taken at that pressure at which the maximum effect was found in helium. Theoretically, there would be no expectation of doubles in hydrogen for the hydrogen atom is pictured as having but one electron and even though hydrogen is diatomic, the chance of catching a double, formed by the electrons being pulled off from each atom, would be negligible, for the positive nuclei remaining, would, presumably, at once repel each other and not be caught together. Commercial hydrogen was used.

Table III.

No. of Pos. Catches.	Press.	t_0.	Av. Interval.	Doubles.	Per Cent.
50.....	26.2	114	64 secs.	1	2
100.....	26.5	95	61	4	4
50.....	27	110	74	0	0
200				5	2.5

Thus hydrogen showed 5 doubles in 200 but since the probability calculation, as given above, would class 4 of these as spurious, it seems fair to conclude that not only were no real doubles secured in hydrogen but, because of the identity of stopping power and the conditions of temperature and pressure, the evidence is confirmed that those secured in helium were real and in no way due to faulty shielding, to the catching of two separately ionized molecules or to any such effects.

Mercury Dimethyl.

The work of Millikan, Gottschalk and Kelly was repeated in this case also but no evidence for real doubles was secured. The delicate adjustment for the end of the range could not be made, in the case of this

poisonous vapor, as with the other gases, so the vapor pressure was raised by raising the room temperature. The multiple relationship between the different valence speeds shown in the first part of the paper proved of great value here as the characteristic speeds constantly changed with the vapor pressure changes.

In conclusion, the writer wishes to thank Professor R. A. Millikan for outlining the problem and for his valuable suggestions during the course of the work. The present paper is but a continuation of Professor Millikan's earlier papers as has been indicated in the references above.

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ANALYSIS OF THE ENERGY DISTRIBUTION IN SPEECH.

By I. B. Crandall and D. MacKenzie.

Synopsis.

The frequency distribution of energy in speech has been determined for six speakers, four men and two women, for a 50-syllable sentence of connected speech, and also for a list of 50 disconnected syllables. The speech was received by a condenser transmitter whose voltage output, amplified 3,000 fold, was impressed on the grids of twin single stage amplifiers. The unmodified output of one of these amplifiers was measured by a thermocouple and was a known function of the total energy received by the transmitter, corrections being made for the slight variation with frequency of the response of the circuit. The output of the other amplifier was limited by a series resonant circuit to a narrow band of frequencies, the energy in this band being measured by a second thermocouple. The damping of the resonant circuit was so chosen that sufficient resolving power and sufficient energy-sensitiveness were obtained over the range from 75 to 5,000 cycles per second; and 23 frequency settings were made to cover this range. For each syllable simultaneous readings were recorded on the two thermocouples at each frequency setting. The consecutive syllables were pronounced deliberately by each speaker, maintaining as nearly as possible the normal modulation of the voice. Corrections were applied to offset the unavoidable variations in total energy incidental to repetition of a given syllable. 13,800 observations were made for all speakers. *The energy distribution curves* obtained are essentially the same for connected as for disconnected speech, and indicate that differences between individuals are more important than variations due to the particular test material chosen. A composite curve drawn from the individual curves shows a great concentration of speech energy in the low frequencies, a result which would not be expected from data previously published by others. The actual results contain a factor due to standing waves between the speaker's mouth and the transmitter, a complication always present in telephoning; this could not be eliminated.

The rate of energy output in speech for the normally modulated voice, was determined from the readings for total energy and was found to be about 125 ergs per second.

In the study of speech and its reproduction by mechanical apparatus it is necessary to consider its composition from several different points of view. We desire first of all to know the actual frequency distribution of the total energy in speech, as well as the separate distributions for each individual sound. We also desire to know the apparent distribution of energy, that is, the distribution as perceived by the ear. Finally we wish to know the importance of each frequency, that is, the contribution to "articulation" or "quality" in the exact reproduction of speech which can be traced to the energy of each elementary band of frequencies in the speech range. In all three cases certain frequency

functions are used to represent these distributions. The advantage of considering these different frequency distribution functions separately has already been indicated by one of the present writers.[1]

In our judgment the most important of these data of speech study is the *actual energy distribution*, considering speech as "a continuous flow of distributed energy" in accordance with the ideas expressed in the earlier paper. The present paper offers a determination of this fundamental factor.

To determine the energy distribution in speech to a high degree of accuracy it would be desirable to analyze a certain amount of connected speech and take a time average of the energy distribution of the whole. This is not feasible at the present time, but a very close approach to this result has been made. The method consists in analyzing the speech waves as impressed on a condenser transmitter, using a tuned circuit to transmit narrow frequency bands of energy and pronouncing the separate syllables of the connected speech so slowly that the kick of a direct current galvanometer connected to an A. C. thermocouple can be separately read for each syllable. Using a suitable calibration for the whole apparatus, the magnitude of this kick can be interpreted in terms of the time integral of the energy at a particular frequency setting for each syllable. A mean of the readings for all the syllables in the "speech" at any frequency setting gives the relative energy at that frequency.

The present method is a modification of an earlier method in which approximate analyses of speech sounds were made, using a condenser transmitter, tuned circuit, an amplifying-rectifying circuit, and ballistic galvanometer. The method is, however, much improved as we now have very accurately calibrated condenser transmitters of better design,[2] and a great deal of care has been taken to calibrate the successive elements of the train of apparatus, and increase the resolving power.

Experimental Procedure.

Sound waves emitted from the mouth of the speaker are allowed to fall upon the diaphragm of a condenser transmitter, connected in the conventional manner to the input of a three-stage amplifier. The output of this is impressed upon the input circuits of twin single stage amplifiers, potentiometers being interposed to permit regulation of the grid voltages of the twin amplifier tubes.

The output circuits of the fourth stage consist of the high windings of two step down ironclad transformers. These step down transformers

[1] "The Composition of Speech," Phys. Rev., X., p. 74, 1917.

[2] The present design of the condenser transmitter and its calibration are fully treated in a paper by Dr. E. C. Wente which will appear shortly in this Journal.

have a voltage ratio of 11 : 1 and are designed to work between impedances of 6,000 and 50 ohms. The low impedance winding of one of these transformers operates into a thermocouple heater of, roughly,

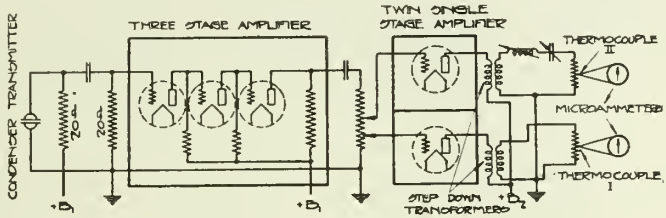

Fig. 1.

Circuit used for the analysis of speech. (The usual details of the three stage amplifier are not shown.)

40 ohms resistance. The low side of the other transformer operates through a tuned circuit into a similar thermocouple heater. The diagram of Fig. 1 exhibits the essential features of the electrical circuits just described.

When the diaphragm of the condenser transmitter is set in vibration by speech a current made up of a range of frequencies flows in the heater of thermocouple I., while the heater of thermocouple II. is traversed only by such a band of frequencies as the resonant circuit allows. Fig. 2 shows a number of typical resonance curves obtained in the course of

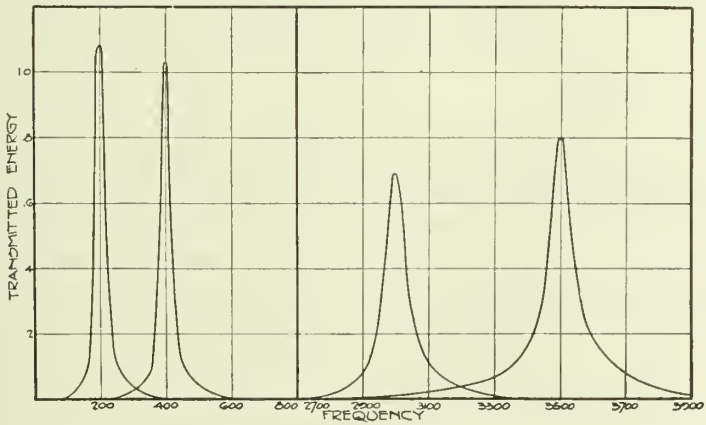

Fig. 2.

Resonance curves showing the resolving power of apparatus.

calibrating this apparatus. These curves are such that the tuned circuit functions as a filter transmitting only a narrow region of frequencies. One side of the twin amplifier transmits the entire electrical response of

the system; the other side suppresses all save a band of frequencies, the center of this band being shifted by resetting the condenser and inductometer.

Having chosen for analysis a piece of connected discourse, the speaker utters the successive syllables separately but as nearly as may be with the same inflection and volume as if the syllables were continuously spoken. Two observers record the readings of microammeters in the couple circuits of the thermocouples. One of these instruments gives a deflection corresponding to the total energy of the syllable uttered; the deflection of the other instrument corresponds to the energy of the syllable lying within the limits of transmission of the tuned circuit.

Preliminary experiments were carried out to determine the relation between momentary deflection read on the microammeter, and the current momentarily flowing in the thermocouple heater. Currents of different values were caused to flow for intervals of time varying from 0.2 second to 1.2 seconds, and the deflections were found nearly proportional to the product of current squared and time interval; this proportionality was most nearly exact when the current was weak and the time intervals short. For all cases likely to be duplicated in the speech analysis work the error might be taken as about 5 per cent., a quantity small in comparison with the inevitable uncertainties due to other causes.

Quite low damping is attained in the resonant circuit. The values of inductance used range from 0.20 to 0.66 henry and the total resistance of the circuit—transformer winding, inductometer coil, thermocouple heater—is of the order of 100 ohms. The damping thus ranges from 75 to 250.

The circuit is calibrated in the following manner:

A switch is so introduced that it is possible to include in series with the thermocouple, the resonant circuit, or replace it by a non-inductive resistance whose value is approximately that of the A. C. resistance of the inductometer winding. With the tuned circuit excluded, an alternating current of suitable magnitude is caused to flow in the thermocouple heater; the tuned circuit is then substituted and the new value of the current observed, the input voltage remaining constant. The ratio of current squared "tuned circuit in" to current squared "tuned circuit out" is plotted against frequency, yielding a curve for energy transmission.

Twenty-three bands in all were considered adequate for the analysis of energy distribution in speech; the centers of these were at 75, 100, 200, 300 cycles, 400 to 3,200 cycles by steps of 200; 3,500, 4,000, 4,500, 5,000 cycles per second. Beyond 5,000 cycles per second, the energy is

so low as to be impossible of measurement with the apparatus used. A Weston Type 322 microammeter recorded the couple current for the tuned circuit side of the twin single stage amplifier. With this instrument and the thermocouple used, 0.2 microampere in the couple circuit corresponds to one quarter of a milliampere in the heater, and this is the lowest readable deflection of the Weston instrument.

Reduction of Observations.

Three corrections have to be made, the first being the correction for varying volume.

Simultaneous observations are made, at each setting of the tuned circuit, of the filtered and the unfiltered energy of each syllable. It is not possible to utter a given syllable with the same intensity and at the same distance from the transmitter for every one of twenty-three times. Accordingly, the "unfiltered" readings are averaged and each of the filtered readings for each syllable reduced from the value actually observed to the value that would have been read had the volume and distance been such as to give the average "unfiltered" reading. This procedure is quite legitimate if it be granted possible to maintain a definite composition of the syllable in question throughout the changes of the tuned circuit setting.

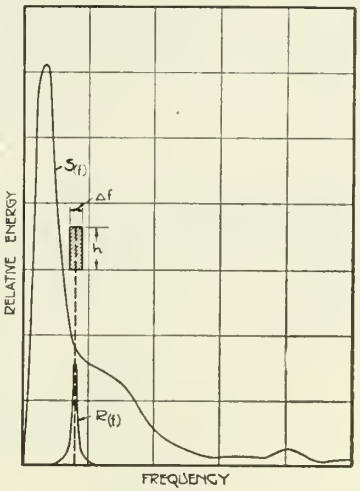

Fig. 3.

Illustrating correction of observations, necessary because of variation in resolving power with frequency setting.

A second correction was made for the varying area of tuned circuit curves.

In Fig. 3 let $S(f)$ be the speech spectrum determined by ideal methods; "R" the transmission curve of the tuned circuit, set for a resonant frequency f. An ideal transmission curve would be a rectangle when plotted in this figure, of height "h" and transmission range Δf.

The true amount of energy $S(f)$ associated with frequency f, and the experimentally determined value which we may call $S(f)$ are connected by the relation

$$h\bar{S}(f)\Delta f = \int_{f}^{f+\Delta f} S(f)R(f)df$$

and if we make

$$h\Delta f = \int_{f}^{+\Delta f} R(f)df$$

we may take for all practical purposes $S(f) = \overline{S}(f)$, considering the narrowness of the transmission range. We must therefore find the factor $h\Delta f$, proportional to the area of each tuned circuit curve and divide the energy received through the filtered side by $h\Delta f$, in order to obtain $S(f)$. This treatment may be gone through for each syllable individually, but it is more convenient to sum the tuned circuit readings for all the syllables used, corrected one at a time for varying volume, and then apply the curve area correction to this sum.

A third correction was made for the varying frequency-sensitivity of the whole apparatus. Thus far we have discussed only the electrical energy in the output circuit of the fourth stage. It remains to show in what way this is related to the mechanical energy of the diaphragm, and this in turn to the incident sound energy.

The calibration of the circuit as a whole was made by introducing a small resistance carrying alternating current in series with the condenser transmitter, thus introducing a known potential drop in the undisturbed input mesh of the circuit.

An amplification curve is appended (A, Fig. 4) which gives to an arbitrary scale the ratio of volts output to volts input as a function of frequency, for the system as actually operated. The calibration of the condenser transmitter, shown in Fig. 4, Curve C, gives the open circuit

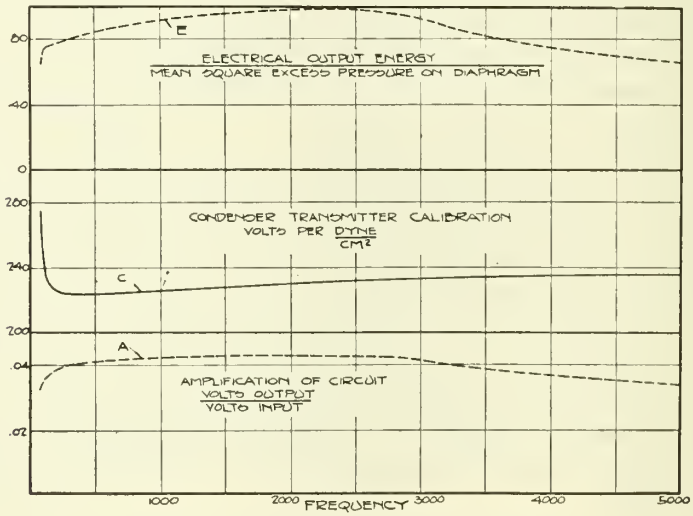

Fig. 4.

Energy-frequency characteristics of the apparatus.

voltage of the transmitter per unit pressure on the diaphragm, as a function of frequency. The product of these curves is the volts output

per unit alternating pressure on the diaphragm, and the square of this product, curve E is proportional to the electrical energy output per unit sound energy incident on the diaphragm, if we assume that the sound energy is proportional to the square of the alternating pressure. This point, however, requires some further discussion, which will be given later on.

It is plain from curve E that the response of the system is a maximum for frequencies in the neighborhood of 2,250 cycles. If, now, the observations already corrected for varying volume and for area of resonance curves, are subjected to further correction for the exaggeration of these frequencies, it is possible to draw a curve which shall exhibit the mean square of the excess pressure on the diaphragm, as a function of frequency in the voice exciting the vibration. We obtain this corrected curve by dividing the results, after the first and second corrections above have been made, by the ordinates of curve E.

Observations.

In order to investigate the possibilities of this method it was decided to work with a rather short piece of connected speech, and to use a limited

Fig. 5.

Analysis of individual voices.

number of observers, on account of the large number of observations which are required for each separate syllable. With six speakers (four men and two women) each pronouncing the test sentence of fifty syllables for each of the twenty-three frequency settings, 6,900 separate observa-

tions were required. It is believed that representative results have been obtained from these observations, but if this is not the case then some method of graphical registration of the energy-time curve of speech for the different frequency settings must be applied in order to handle the vast amount of data involved in work on an appreciably larger scale.

The test sentence used was as follows:

"*Quite* four score and seven years ago our fathers brought forth on this continent, a *nice* new nation, conceived in liberty, and dedicated to the proposition that all men are created equal."

The two *italicized* words were added to the first sentence of the "Gettysburg Address" in order to bring the total up to fifty syllables, and improve the balance between the vowel sounds.

The resulting speech-energy curves are shown in Figs. 5, 6 and 7,

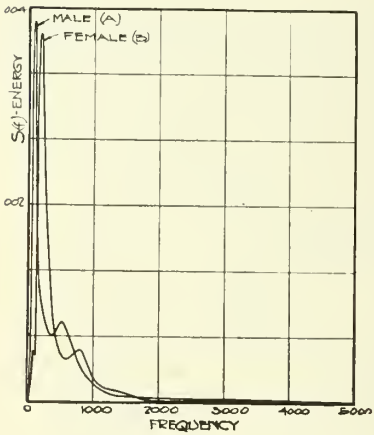

Fig. 6.

Energy distribution: composite curves of male and female voices.

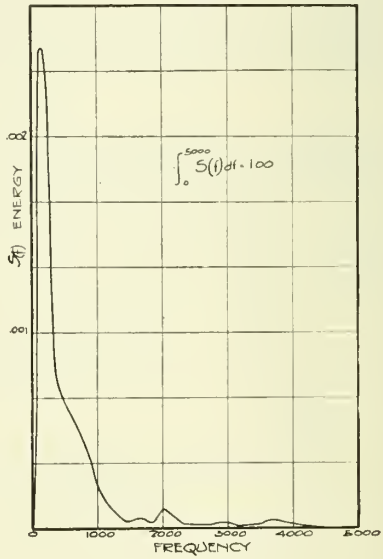

Fig. 7.

Energy distribution: composite curve for all voices.

plotted so that $\int_0^\infty S(f)\,df = 1$ in each case. In Fig. 5 the individual curves for each of the six speakers are shown on a small scale; in Fig. 6 the composite curve for the men and the composite curve for the women, drawn separately, and in Fig. 7 the composite curve for all six speakers, giving the data of curves 6*A* and 6*B* equal weight.

These curves are very similar to a curve obtained by Dr. Fletcher of this laboratory, using block filters and based on the simple calling sentence "Now we're off on one." A general consideration of this fact and of

the data shown leads us to believe that the differences between curves of this sort, made by the method described are due rather more to differences between the voices of the individual speakers than to the particular piece of connected speech which is chosen, provided the speech is of reasonable length. The differences between the different voices are so marked that we should expect them to remain even though we used as test material a connected speech ten or fifty times as long as the sentence used.

The Energy Distribution in Speech.

An interesting comparison may be made between the curves shown for the energy distribution of "continuous speech" and certain speculative curves previously constructed to indicate the energy distribution. One of these curves is shown in Fig. 8. Curve *A* was constructed by one

Fig. 8.

Energy distributions: *A*. Synthesized from vowel records of D. C. Miller (1916). *B*. Disconnected speech analysis of this paper. *C*. Connected speech analysis of this paper (from Fig. 7).

of the writers in 1916 in an attempt to synthesize the energy curve from the energy distributions of the vowel sounds, using the vowel analyses of Dr. Dayton C. Miller. Curve *C* is the composite "continuous speech" curve of Fig. 7. The vowel sounds analyzed by Miller were intoned and the vowel sounds analyzed by us were spoken, but Miller's work seemed to show that there was no essential difference between intoned and spoken vowel sounds. There is, however, a very noticeable difference between

Curve *A* and Curve *C*, the energy in the fundamental tone of the speaker's voice coming out much more strongly in Curve *C*. We should expect that our improved apparatus would record the energy in the lower frequencies more correctly than the apparatus heretofore used but as we used different test material (connected speech instead of disconnected syllables or vowel sounds) it is not immediately evident which of these two factors is responsible for the differences between the *A* and the *C* curves.

In order to investigate this point more fully the testing routine for all six speakers was repeated, using instead of the fifty-syllable sentence, the fifty disconnected syllables of one of the standard articulation testing lists, as used by Dr. Fletcher in this laboratory. The results for energy distribution are shown in Fig. 9, Curve *A* being the mean energy distribution for the four male speakers, using the syllables, while Curve *B* is the mean energy distribution for the two female speakers. Curves 9*A* and 9*B* may be compared with Curves 6*A* and 6*B* which represent the sentence of continuous speech. The two sets of curves are essentially the same as shown in Fig. 8, *C* and *B* being respectively the composite curves for all speakers, using connected and disconnected speech.

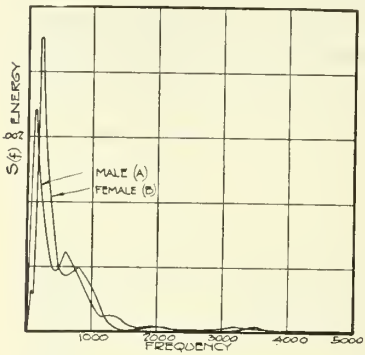

Fig. 9.

Energy distribution in disconnected speech.

Such small differences as exist between Curves *C* and *B* of Fig. 8 may probably be due to differences in the distribution of the vowel sounds in the connected and disconnected test material. This distribution is given in the following table:

Vowel Sounds.	a	ā	á	e	ē	ér	i	ī	o	ō	ó	u	ū	ou	Total
In Sentence	6	6	3	7	3	3	7	2	2	5	3	0	2	1	50
In Syllabic List (No. 174)	4	4	3	4	3	4	3	4	3	4	3	4	4	3	50

Key to Vowel Sounds: a, as in father (or o as in top); ā, as in tape; á, as in tap; e, as in ten; ē, as in team; ér, as in term; i, as in tip; ī, as in time; o, as in ton; ō, as in tone; ó, as in for; u, as in pull; ū, as in rule; ou, as in house

The similarity between Curves C and B of Fig. 8 is evidence of the general reliability of the method, and leads to two rather important conclusions.

In the first place, characteristic results have been obtained for a given set of speakers, using two different types of test material. This seems to show that the choice of test material does not require especial consideration, provided it is of sufficient length. It seems to be a matter of rather greater importance to increase the number of observers.

In the second place, it seems that for the actual energy distribution, the results previously obtained from the vowel analyses are definitely in error, in that they show relatively little energy associated with the lower voice frequencies.

Criticism of the Results.

The foregoing treatment provides a curve showing the frequency distribution of the square of the excess pressure on the diaphragm.

In an undisturbed field of sound energy we have for the intensity

$$I = \frac{P^2}{2\rho a}$$

in which ρ is the mean density of the medium, a the velocity of sound in the medium and P the maximum excess pressure.

It remains for us to consider in how far the results obtained represent the frequency distribution of sound energy in speech.

Due to the fact that at frequencies where the sound wave-length is short and comparable with the diameter of the transmitter, considerable reflection takes place, and the pressure on the diaphragm is proportionately greater for these frequencies than for those which are not accompanied by strong reflection. In this respect again the higher frequencies provoke the greater response in the system.

The following experiment was tried to investigate this variation. A wall six feet square, with a central hole to fit over the condenser transmitter, was brought up to make the transmitter a part of a plane wall. The clearance around the periphery of the transmitter was tightly closed, and reflection was to be expected at all frequencies. Where total reflection takes place, a given quantity of sound energy results in twice the alternating pressure on the diaphragm as when no reflection occurs. That is, the resulting electrical energy observed should be four times as great for total reflection as for no reflection. The wall was expected to cause reflection at all frequencies, and the experiment consisted in reading the electrical response, with and without the wall, the condenser transmitter being exposed to tones of frequencies from 200 to 10,000

cycles per second under definite adjustments of the supply circuit of a receiver producing this tone. When the frequency is low, little reflection takes place from the transmitter standing alone, and bringing up the wall should cause a great increase in the response of the system. At high frequencies the transmitter should reflect nearly as much alone as when part of a large wall, and the readings with and without the wall should be nearly equal. Plotting ratio of response without, to response with the wall was expected to yield a curve which could be used to make the final reduction of electrical output to incident sound energy, and so permit a more accurate determination of the spectrum of sound energy of the voice.

No consistent results were obtained after several trials and the experiment was abandoned. The failure is doubtless to be ascribed to standing waves, the character of which is very sensitive to the location in the room of the transmitter and the wall. This experiment is to be repeated under more favorable conditions when standing waves can be eliminated.

Thus, the curves finally obtained show no more than the frequency distribution of energy in speech in terms of the mechanical energy of a more or less ideal transmitter diaphragm. However, this information has its value because in any given configuration of transmitter, speaker, and room, there is a definite correspondence between the sound energy of the voice and the force acting on the diaphragm on which it falls, and in telephony at any rate it is this action on the diaphragm with which we are immediately concerned.

In conclusion we may give a determination of the total energy rate of speech, obtained as a by-product of the preceding investigation. Knowing the calibration of the system in absolute units, it is possible to determine the alternating pressure on the condenser transmitter diaphragm exposed to continuous speech from the normally modulated voice under the conditions of the experiment. Using the mean of the values obtained with 9 observers we find for the alternating pressure 11.3 dynes per sq. cm. (r.m.s.) for a distance of 2.5 cm. from mouth to diaphragm. This corresponds to an energy flow of 3.2 ergs per sq. cm. per second. Assuming that this energy flow is distributed uniformly over a hemisphere of 2.5 cm. radius, we may take 125 ergs per second as the total sound energy flow from the lips with the normally modulated voice.

RESEARCH LABORATORY OF THE
AMERICAN TELEPHONE AND TELEGRAPH CO.,
AND THE WESTERN ELECTRIC CO., INC.

NOTE ON THE DISTRIBUTION OF RANGE OF RECOIL ATOMS.

By K. T. Compton.

Synopsis.

Number and Range of Recoil Rays, Produced by α-ray Bombardment, to be Expected on the Assumption of the Inverse Square Law of Force between Nuclei.—In calculating these quantities for comparison with his experimental results for hydrogen, Rutherford took account only of impacts occurring at the slit, whereas recoil rays may reach the screen from other points. In this note is given a method of calculating the exact number of recoil rays, for a given thickness of absorbing screen, to be expected with the experimental arrangement used for gases by Rutherford. The results for hydrogen come out about 30 per cent. larger than those computed by Rutherford; but this fact does not invalidate his conclusion that the difference between experimental and theoretical curves indcates a law of force other than the inverse square in the case of collisions by high speed α particles.

In his paper on the collision of α particles with atoms of hydrogen,[1] Professor Rutherford has shown that, at the smallest distances between hydrogen nuclei and the fastest α particles, the force is no longer that of the simple inverse square, due probably to additional forces arising from the distortions of the nuclei. This conclusion was drawn from the observation that, for the fastest α particles, a larger proportion of the recoil atoms is projected with high velocity in the direction of impact than is predicted from theoretical considerations based on the inverse square law. The theoretical equation used does not correspond exactly to the actual experimental conditions, since it applies to a case where all the recoil atoms come from impacts occurring at the slit, whereas, in the actual experiments, recoil atoms come from certain regions in the volume of the gas as well as from the gas at the slit. More recently Professor Rutherford has called attention to this inaccuracy in his original treatment of the problem,[2] and Darwin[3] has indicated a method of correctly deducing, from experiments on the distribution of range of the recoil atoms, the nature of the force at the collision.

The present note outlines a direct and easy method of calculating the exact distribution of range to be expected with an experimental arrangement of the type used for gases, if the inverse square law of attraction holds true. It is, therefore, a special case of the problem treated by

[1] Phil. Mag., 37, p. 537, 1919.
[2] Phil. Mag., 41, p. 307, 1921.
[3] Phil. Mag., 41, p. 486, 1921.

Darwin, but is in a form convenient in application to cases where it is desired to detect departures from the inverse square law. Although a correction to Professor Rutherford's calculations, the result of the present treatment shows that the validity of his conclusions is in no way vitiated. Even the corrected calculations are far from agreeing with the experimental results, which shows that the law of force at the collisions of very high speed α particles with atoms is not that of the inverse square.

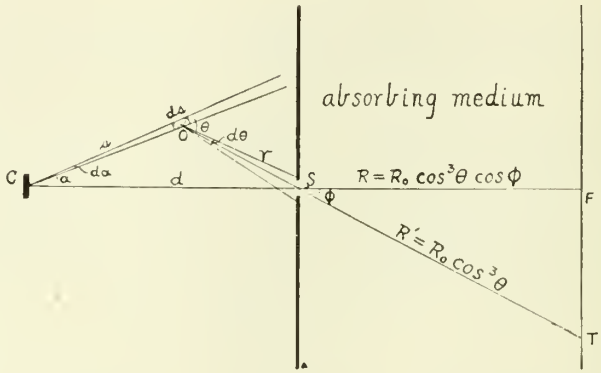

Fig. 1.

α particles leave the point C, traveling in all directions. The number of these leaving per second is N'. Of these,

$$Q = \frac{N'A}{4\pi d^2}$$

pass through the slit S, of area A at a distance d from C. Beyond S they pass through a slab of absorbing material of thickness equivalent to R centimeters of air, and strike the fluorescent screen F.

If hydrogen fills the region to the left of the slit, recoil atoms may be produced at any point O, and some of these will pass through the slit. They will strike the fluorescent screen if their velocity is sufficient to give them a range greater than the distance ST through the absorbing screen. The number n per second of these scintillating recoil atoms is counted, when the absorbing screen is more than thick enough to stop the α particles.

$\frac{1}{2}N' \sin \alpha d\alpha$ is the number of α particles leaving C in directions between α and $\alpha + d\alpha$ per second.

$2\pi N\mu^2 \tan \theta \sec^2 \theta d\theta$ is the fraction of the α particles which, in one centimeter path, produce recoil atoms at angles of recoil between θ and $\theta + d\theta$. Here N is the number of gas atoms per unit volume and

$$\mu = \frac{eE}{v^2}\left(\frac{1}{m} + \frac{1}{M}\right),$$

where e, E, m and M are the charges and masses of the recoil atom and α particle, and v is the velocity of the α particle.

$A \cos \phi / 2\pi r^2 \sin \theta d\theta$ is the fraction of the recoil atoms, produced at O and starting in directions between θ and $\theta + d\theta$ with s, which pass through the slit.

Therefore, the product of these quantities leads to

$$n = \int_{\alpha=0}^{\alpha=\pi/2} \int_{s=0}^{s=s'} \tfrac{1}{2} N'NA\mu^2 \sin \alpha d\alpha \frac{\cos \phi}{r^2 \cos^3 \theta} ds$$

as the total number of recoil atoms passing per second through the slit, where s' is so chosen that the recoil atom has such velocity and direction as to enable it just to reach the fluorescent screen.

Equations relating certain of the above quantities are

$$s \sin \theta = d \sin \phi,$$
$$r \sin \theta = d \sin \alpha,$$
$$\theta = \alpha + \phi,$$

by use of which the above equation may be written

$$n = \int_{\alpha=0}^{\alpha=\pi/2} \int_{\theta=\alpha}^{\theta=\theta_1} \tfrac{1}{2} N'N \frac{A}{d} \mu^2 \left(\frac{\cos \alpha}{\cos^2 \theta} + \frac{\sin \alpha \sin \theta}{\cos^3 \theta} \right) d\alpha d\theta,$$

where θ_1 is the largest angle of recoil at which the recoil atoms may reach the absorbing screen.

The integration with regard to θ gives

$$n = \int_0^{\pi/2} \tfrac{1}{2} N'N \frac{A}{d} \mu^2 \left(\tan \theta_1 \cos \alpha + \frac{\sin \alpha}{2 \cos^2 \theta_1} - \sin \alpha - \frac{\sin \alpha}{2 \cos^2 \alpha} \right) d\alpha.$$

The limiting value θ_1 is determined by the relation $R = R_0 \cos^3 \theta_1 \cos \phi_1$, where R_0 is the maximum range of the recoil atoms and R is the equivalent thickness of absorbing medium, since the range measured normally through the absorbing screen is proportional to the cube of the velocity of recoil and to $\cos \phi$. This may be written

$$R/R_0 = \cos \alpha \cos^4 \theta_1 + \sin \alpha \cos^3 \theta_1 \sin \theta_1$$

and the value of θ_1 corresponding to any specified range R of the recoil atom may thence be calculated for any desired value of α.

The last integration is made graphically by evaluating first θ_1 and then the expression in parenthesis, for various values of α (R being fixed), plotting the values of the expression against α and taking the area under the curve. When this is done, and the known values of μ and N are substituted, and $4\pi Qd^2$ is substituted for $N'A$, the value of n/Qd is found for the particular value of R chosen. This process may then be repeated for other values of R.

In Fig. 2, the solid line shows the values of n/Qd for different values of R, calculated in the manner outlined above. The broken line shows the values calculated by the approximate equation used by Professor Rutherford. Both curves refer to recoil atoms produced by α particles whose range in air is 7 cm.

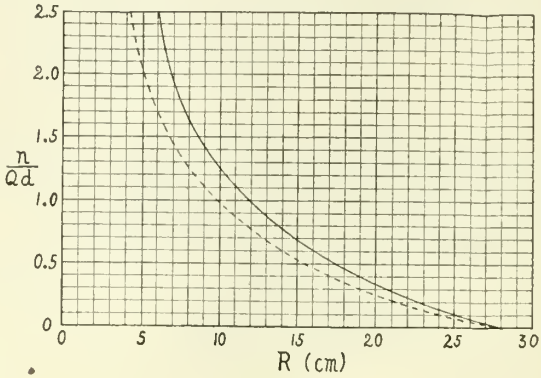

Fig. 2.

Since Professor Rutherford's conclusions regarding the nature of the forces at collision are drawn from a great difference between the shapes of the theoretical and the experimental curves for high velocity α particles, it is evident that they would not be modified by substituting the exact for the approximate theoretical distribution. For relatively slow α particles, however, the number of scintillations observed agrees better with the theoretical predictions as calculated above than with those calculated by the approximate equation, since Professor Rutherford found the observed number to be always somewhat greater than that calculated by the approximate equation. The present work indicates that the theoretical numbers should be uniformly about 30 per cent. larger than those calculated by Professor Rutherford.

PALMER PHYSICAL LABORATORY,
PRINCETON, NEW JERSEY.

THE VARIATION WITH THE TEMPERATURE OF THE THERMAL CONDUCTIVITY OF CAST IRON.

By Elmer E. Hall.

Synopsis.

Variation with Temperature of the Thermal Conductivity of Soft Gray Cast Iron, 195° to 542° C.—The sample used contained 3.5, 2.2 and 0.64 per cent. of C, Si and Mn respectively, and was cast into the form of a cylindrical shell 3 cm. thick, joined with a hemi-spherical bottom. The temperature differences between the liquids inside and outside the shell, which amounted to from 3° to 6° with an input of from 0.24 to 1.6 kw, were measured with thermo-couples silver-soldered in the ends of brass tubes. Since even though these tubes were pressed against the iron surfaces, the temperatures thus measured differed more or less from the actual temperatures of the surfaces, the absolute values found for the conductivity are too low; but the results indicate that the conductivity at 542° is between 2 and 3 times its value at 195° C.

It was discovered in 1852 by J. D. Forbes (Atheneum, p. 102, 1852) that the thermal conductivity of iron was different at different temperatures. Investigations since that date have seemed to establish the fact that the conductivity of pure wrought iron decreases while that of cast iron increases with rise of temperature. This paper gives the results obtained for a specimen of soft cast iron as used in stove castings, the specimen being cast by the San Francisco Stove Works. Professor W. C. Blasdale of the chemistry department of the University of California has determined the silicon (Si) and manganese content to be 2.19 and 0.64 per cent. respectively. The carbon content was approximately 3.5 per cent.

The form of the specimen was that suggested by Mr. Carl Hering (Trans. Am. Electrochem. Soc., 18, p. 213, 1910), being a cylindrical shell with one end capped with a hemispherical shell. The dimensions of the casting were as follows: length of the circular cylindrical shell, 25.2 cm. inner diameter 6.0 cm., outer diameter 12.0 cm. The inner and outer diameters of the hemispherical cap were 6.0 and 12.0 cm. respectively. The casting was well made and after being cleaned in the lathe the thickness of the wall as measured at different points varied from 3.0 cm. by less than one per cent.

The specimen was immersed in a bath in a vessel of the same shape as the specimen. The temperature of this outer bath was subject to control as the outer vessel was provided with both a heating and a

cooling coil. The interior of the specimen was filled with an electrically heated bath. Heat losses at the open end of the cylinder were prevented by keeping the temperature and temperature gradient immediately over the specimen and baths closely the same as that of the baths themselves. This was done by auxiliary heating coils, thus constituting a modified guard ring scheme. The heating element in the bath inside the specimen consisted of a graphite rod $\frac{5}{16}$ of an inch in diameter, inside a $\frac{1}{2}$ inch iron pipe, contact at the bottom of the pipe between pipe and rod being secured by having a little molten lead in the cap of the iron pipe. Asbestos string wound every few inches along the graphite rod prevented warping of the rod and insured sufficient electrical insulation. The upper ends of both the rod and the pipe were joined to heavy copper leads. The measurement of the difference in potential between the proper points in the heater system, together with the current used, gave means of determining the energy input, the power factor for this type of conductor being unity. Alternating current from a variable voltage step down transformer was used.

The temperature of the walls of the specimen was measured with four pairs of copper-constantin thermocouples, placed at various depths. The thermocouples were calibrated, using the boiling points of water, naphthalene and sulphur, the cold junctures being kept at 20° C. The thermocouples were made from No. 28 wire and special care was given to their construction. A small bulge was made near the end of a thin walled brass tube, the tube being about 4 mm. in diameter. The wires for a thermocouple, after being well annealed and joined with silver solder, were insulated with pieces of fine hard glass tubing. The couples were then inserted in the brass tube and the juncture drawn through a small hole in the center of the bulge until the glass insulation was tight against the inner wall of the tube and the juncture was in the wall of the thin brass tube. The opening was then closed with silver solder and the protruding wires cut. The end of the brass tube was then closed with a layer of asbestos and a brass plug, the union being made tight with silver solder. When in place the center of the bulge in the brass tube, and hence the juncture of the thermocouple, was pressed against the surface of the specimen. Both baths were vigorously stirred and the thermocouples gave the same readings irrespective of their depths.

Assuming radial flow of heat, mathematical analysis readily gives for this form of specimen,

$$k = \frac{aw}{Jt};$$

where k is the thermal conductivity in gram calories per deg. per cm. per sec.; w is the electrical power in watts transformed into heat within the specimen; J is the mechanical equivalent of heat; t is the fall in temperature through the wall of the specimen; and a is a constant depending on the dimensions of the specimen. It can be shown that

$$a = \frac{e \, ln \frac{D}{d}}{\frac{\pi}{2} dDln \frac{D}{d} + 2\pi Le},$$

e denotes the wall thickness, D the outside and d the inside diameter, L the length of the cylindrical part, ln stands for the natural logarithm. Inserting the dimensions of the specimen as given above and combining a and J we have

$$k = 0.000897 \, wt.$$

For temperatures below 300° C. the baths were paraffin and above this temperature the baths were lead. The readings were made by O. R. Hull and O. S. Imhoff, working independently and about one year apart; each man making a complete new set up, including new thermocouples. It took from fifteen to thirty hours to obtain constant conditions. Readings were not accepted until conditions, as determined by the readings, had remained practically constant for at least one hour. Readings were then recorded every minute for twenty minutes and the mean taken. Since power line current was used there was a slight fluctuation in input. This fluctuation was cared for by taking most of the readings at night, and by extending the readings over a twenty-minute period, the instruments being carefully watched for the hour preceding. The results are given in the following table.

Amperes.	Volts.	Watts.	Inside Temp. C.	Outside Temp. C.	Difference t.	Mean Temp.	Conductivity k.	Thermal Ohms.	Observer.
80.....	3.00	240	197	194	3.0	195.5	0.0718	3.32	H.
81.25...	3.00	243.75	199	196.1	2.9	197.6	.0754	3.17	I.
120.....	3.50	420	287.2	283.3	3.9	285.3	.0965	2.47	H.
108.....	3.32	358.56	287	283.7	3.3	285.4	.0975	2.45	I.
120.....	3.50	420	296.8	293.1	3.7	298.6	.1018	2.35	H.
125.....	4.89	611.25	405.2	401.4	3.8	403.3	.1443	1.66	I.
128.....	5.00	640	426.6	422.9	3.7	424.8	.1552	1.54	I.
135.....	5.51	743.85	445.0	440.8	4.2	442.9	.1589	1.50	I.
165.....	6.99	1,153.35	506.5	501.1	5.4	503.8	.1916	1.25	I.
178.....	7.30	1,299.40	528.7	523.0	5.7	525.9	.2044	1.17	I.
200.....	7.91	1,582	545.2	538.6	6.6	541.9	.2050	1.16	I.

The method is open to the objection applicable to all cases where measuring the temperature of a surface is involved. What is doubtless measured in every such case is the temperature slightly away from the surface. Since the thermal resistance of the surface film of a substance is greater than for the substance itself, and since the thermal conductivity of lead is less than that of iron, it might be expected that this method would give results slightly low for any given temperature. However the variation of the conductivity with the temperature is believed to be well exemplified.

UNIVERSITY OF CALIFORNIA,
DEPARTMENT OF PHYSICS.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE CHICAGO MEETING, NOVEMBER 25 AND 26, 1921.

THE 111th regular meeting of the American Physical Society was held at the University of Chicago on November 25 and 26, 1921. President Lyman of the American Physical Society presided.

At a meeting of the Council held on November 26 sixty-three persons were elected to *Membership* and two were transferred from *Membership* to *Fellowship*, as follows: *Elected to Membership:* Hilda Begeman, Victor H. Benioff, Lester I. Bockstahler, Robert B. Brode, Detler V. Bronk, James W. Broxon, Walter A. Buchheim, R. R. Chappell, Chien Cha, Tobias O. Chew, H. T. Clifton, J. Fenton Daugherty, Ward F. Davidson, Elmer R. Drew, Arthur R. Duane Jesse Wm. DuMond, J. W. Ellis, Kenneth V. Glentzer, Philip F. Gottling, E. T. Hoch, Paul L. Hoover, R. J. Hopkins, Harold O. Holte, Haidee H. Hoover, B. A. Howlett, Roy J. Kennedy, Freda Kergor, Arthur D. Kinsman, Arthur L. Klein, V. O. Knudsen, Israel Koral, Harold R. Laird, Claude J. Lapp, Marcella Lindeman, Edward M. Little, Elsie J. McFarland, Robert C. Matlock, Edna L. Meacham, Yi-Ch'i Mei, Charles F. Mercer, L. G. Morell, Larrance Page, Wellington A. Parlin, Thomas J. Parmley, Donald MacLean Purdy, P. S. Olmstead, Carl A. Richmond, F. L. Robeson, Glenn F. Rouse, Harvey C. Roys, Arthur E. Ruark, C. Arthur Smith, John E. Smith, William O. Smith, William G. Spandon, Ralph B. Spence, W. W. Steffey, Elbridge Z. Stowell, Philip Subkow, L. W. Taylor, Irving Wolff, Raymond F. Yates, Charles T. Zahn; transferred to *Fellowship:* G. M. Moffit and John K. Robertson.

The following program of forty-four papers was presented, eight being read by title.

Molecular Models: Benzene. JARED KIRTLAND MORSE.

The Mobilities of Electrons in Pure N_2. LEONARD B. LOEB.

On the Pressure Increase in the Corona Discharge. JAKOB KUNZ.

The Vibration of Wires in the Corona. CHARLES S. FAZEL.

The Path of a Rigid Electron Moving in a Magnetic Field of Constant Strength Rotating with Constant Angular Velocity. E. O. HULBURT.

The Effect of Ageing on the Secondary Electron Emission from Copper Surfaces. L. E. MCALLISTER.

Carbon Dioxide Band Spectra in the Near Infra-red. E. F. BARKER.

Recent Determinations of the Susceptibilities of Oxygen and Nitric Oxide and the Magneton. E. C. FRITTS.

The Growth and Decay of Photo-Thermionic Currents from Oxide Coated Filaments. H. D. ARNOLD and HERBERT E. IVES.

The Absolute Sizes of Certain Monovalent and Bivalent Ions. WHEELER P. DAVEY.

On the Universal Distance of the Order of 10^{-8} centimeters, between the Centers of the Nearest Atoms in Solids. ALBERT C. CREHORE.

The Classification and the Prediction of Isotopes. WILLIAM D. HARKINS.

The Nature of Charcoal "Sorption." H. HORTON SHELDON.

The Scattering of Electrons by Nickel. C. DAVISSON and C. H. KUNSMAN.

Width of Spectral Lines of Helium as a Function of Pressure in the Source. LLOYD W. TAYLOR.

On the Vacuum Spark Spectrum of Silicon. R. A. SAWYER and R. F. PATON.

The Sparking Potential in Argon at Reduced Pressures. E. R. STOEKLE.

The Action of Light on a Photographic Film. JAY W. WOODROW.

The Instructional Value of Certain Types of Motion Pictures. HARVEY B. LEMON.

Sensibility of the Ear to Small Differences in Intensity and Frequency. V. O. KNUDSEN.

The Efficiency of Artificial Aids to Hearing. PAUL E. SABINE.

Doppler's Principle Illustrated by Ripple Waves. F. R. WATSON and W. B. WORSHAM.

Einstein's Relativity and Gravitation. JOHN MILLIS.

Some Aspects of the Theory of Relativity. A. C. LUNN,

Atomic Constants and Dimensional Invariants. A. C. LUNN.

Measurements of the Amount of Scattered Homogeneous X-Rays of Wavelength 0.712Å. per Gram of Carbon. C. W. HEWLETT.

The Spectrum of Secondary X-Rays. ARTHUR H. COMPTON.

Oscillations of Temperature of an Incandescent Filament, and the Specific Heat of Tungsten. K. K. SMITH and P. W. BIGLER.

Effect of Tension on Thermoelectromotive Forces by Magnetization. ALPHEUS W. SMITH.

Positive Ray Analysis of Lithium and Zinc. A. J. DEMPSTER.

A Convenient Contactor for Small Currents. FREDERICK J. SCHLINK.

The Dielectric Constant of Mica. J. R. WEEKS, JR.

A Photomicrographic Study of a Series of Drawn Tungsten Wires. L. P. SIEG.

A Simplified Method of Correcting for the Decrement of a Decremeter. R. R. RAMSEY.

A New Visual Null Method for Conductivity Determination. FABIAN M. KANNENSTINE and ESME E. ROSAIRE.

Phase Relations in Coupled Circuits. N. H. WILLIAMS.

The Change of Mobility of the Positive Ion with Age in Oxygen and Nitrogen. Henry A. Erickson.

Spherical Aberration in Thin Lenses. T. Townsend Smith.

A Low Resistance Connection with a Revolving Shaft. A. P. Carman.

The Effect of Pressure and Gas Content on the Action of Vacuum Tube Detectors. H. A. Brown and Chas. T. Knipp.

Some Remarks on Electromagnetic Induction. S. J. Barnett.

The Existence of Small Ions of Very High Mobilities. Oswald Blackwood.

Effect of Lunar Gravity upon a Quartz Thread Balance. R. C. Hartsough.

On the Electrical Properties of Illium. Chas. T. Knipp and J. L. Hall.

Henry Crew,
Secretary, pro tem.

Molecular Models: Benzene.

By Jared Kirtland Morse.

It has been found possible to construct a three-dimensional model for a molecule of benzene which is based on its chemical properties, by arranging the carbon nuclei at the corners of a regular octahedron and by placing the hydrogen nuclei along the axes of this geometrical form; three of the hydrogen nuclei being placed at a distance (y) and the remaining three nuclei at a distance (z) from their respective corners of the octahedron whose edge is denoted by (x).

Such a model has three distinctive axes given by the expressions: $2x \cos 45° + 2y$; $2x \cos 45° + 2z$; $2x \cos 45° + y + z$.

It can be shown that the lengths of these axes also are given by the formulæ

$$\sqrt[3]{\frac{na^2\mu}{\rho c N}}; \quad \sqrt[3]{\frac{n\mu}{acN\rho}}; \quad \sqrt[3]{\frac{n\mu c}{\rho a N}},$$

where n denotes the number of molecules common to the elementary space lattice, μ the molecular weight, a and c the crystallographic axial ratios, ρ the density, and N Avrogadro's number. Putting the vaules computed from these formulæ equal to our expressions in x, y, and z, we obtain the equations:

$$\begin{aligned} 2x \cos 45° + 2y &= 7.983 \times 10^{-8} \text{ cm.} \\ 2x \cos 45° + 2z &= 9.979 \times 10^{-8} \text{ cm.} \\ 2x \cos 45° + y + z &= 8.981 \times 10^{-8} \text{ cm.} \end{aligned}$$

By taking $x = 2.514 \times 10^{-8}$ cm. as determined from Bragg's work on the structure of diamond and solving $x = 2.514 \times 10^{-8}$; $y = 2.214 \times 10^{-8}$; $z = 3.212 \times 10^{-8}$ cm.

By constructing models for naphthalene and anthracene and substituting these values in the expressions for their distinctive axes, axial ratios can be predicted which agree within the limits of experimental with the crystallographic measurements of these compounds.

University of Chicago,
November 7, 1921.

The Mobilities of Electrons in Pure N_2.

By Leonard B. Loeb.

In the course of measurements of the constant of attachment of electrons to neutral molecules results were obtained indicating that the mobilities of the electrons in nitrogen were much higher than those given by previous observers. The mobilities of photoelectrons were accordingly determined in pure N_2 gas between pressures of 600 and 75 mm. using the Rutherford alternating current method. The alternating potentials were produced by the high-frequency oscillations of two audion oscillators acting in parallel and ranged from 7,000 cycles to 150,000 cycles per second.

The mobilities thus obtained were many times higher than those obtained by previous observers (*i.e.*, values of about 10,000 cm./sec. volt/cm. were found. They were furthermore not constant when reduced to a pressure of 760 mm. The values reduced to this pressure varied in a definite manner with changes in pressure, plate distance, and voltage between the plates. These variations may be summarized in the following equation for the mobility constant.

$$K = \frac{571{,}000}{21 + 760\,V/pd},$$

where V is the potential between the plates in volts, p is the pressure in mm. Hg, and d is the distance between the plates.

This unexpected variation of K with voltage explains certain peculiarities observed in the shapes of the mobility curves. A careful analysis of the method shows that the possible sources of error cannot account for the results.

The results are compared with the equation for electron mobility proposed by Townsend. This comparison leads one to conclude that the Townsend method of analysis must be abandoned or the following conclusions must be drawn. Either the energy lost by the electron at each impact with the nitrogen molecule is less the greater the energy of the electron, or the mean free path of the electron is some function of its energy. In any case, the mean free paths of the electrons in nitrogen gas must be about 3.9 times the mean free paths of electrons to be expected on the basis of simple kinetic theory, viz., $4\sqrt{2}$ the mean free path of gas molecules.

University of Chicago,
October 31, 1921.

On the Pressure Increase in the Corona Discharge.

By Jakob Kunz.

It is assumed that the electric momentum of the ions in the corona discharge is transferred to the gas molecules, which acquire a mechanical momentum, which makes itself felt as a pressure increase. The ratio of the mobilities of the ions of various gases is calculated and found to agree with the same ratios obtained by measurements in different processes of ionization. A

large amount of heavy ions is present in the corona discharge. The time required for the evolution of the corona pressure is calculated and found to be in agreement with experience. The phenomena of pressure increase in alternating current corona are also explained.

University of Illinois,
November 6, 1921.

The Vibration of Wires in the Corona.

By Charles S. Fazel.

The vibration of wires carrying a sufficiently high potential to show the corona has been reported by a number of observers. This effect takes place in both the direct and alternating current corona. In view of the close relation between the electric wind, the corona pressure, and this type of vibration, the conditions for its production have been studied. Thus far these studies have been confined to the case of an alternating potential between parallel wires.

It has been found that in order to get maximum vibration the natural frequency of the wire must be the same as that of the impressed potential. However it is necessary that the tension on the wire be small. That is the resonance amplitude is larger with smaller tension.

As the voltage is increased the amplitude increases very abruptly but soon reaches a constant value. This value is maintained as the voltage is increased until a critical voltage is reached where another sharp increase to a constant value is observed. The location of this critical voltage depends on the distance between the wires. The final value of the amplitude is maintained until the arc stage is reached.

The relation between the voltage and the amplitude may be explained on Kunz's theory of the corona pressure. In the first stage the vibration of the wire is due to the momentum of the high mobility carriers. When sufficient electric force is available to get the low mobility, heavy carriers across in the time between alternations, their effect is shown by the second stage of the curve.

University of Michigan.

The Path of a Rigid Electron Moving in a Magnetic Field of Constant Strength Rotating with Constant Angular Velocity.

By E. O. Hulburt.

A rigid electron is assumed of mass m and charge e. The reactions on its motion due to finite size, radiation, and the variation of mass with velocity are neglected. The electron is subjected to a magnetic field H which rotates in the XZ plane. The X, Y and Z components of the magnetic field are, respectively, $H \cos \omega t$, o, and $H \sin \omega t$, where $\omega/2\pi$ is the frequency of rotation. Let x, y and z be the positional coördinates of the electron. When Newtonian notation and electromagnetic units are used, the equations of motion of the electron are

$$\frac{m}{e}\ddot{x} = -H\dot{y}\sin\omega t,$$

$$\frac{m}{e}\ddot{y} = H(\dot{x}\sin\omega t - \dot{z}\cos\omega t),$$

$$\frac{m}{e}\ddot{z} = H\dot{y}\cos\omega t.$$

These equations were solved and the constants determined for two sets of initial conditions. Given initially $t = 0$, $x = y = z = \dot{x} = \dot{y} = 0$ and $\dot{z} = W$, the path of the electron was found to be a wavy curve inside of a ring whose axis is parallel to the Y axis. Given initially $t = 0$, $x = y = z = \dot{x} = \dot{z} = 0$ and $\dot{y} = V$, the path of the electron was a rather complicated type of spiral winding in the general direction of the Y axis.

A special case occurs when ω is large. By means of high-frequency alternating current, such as is obtained in electron tube circuits, it is possible to produce magnetic fields which rotate with frequencies of the order of 10^6. When ω is large the positional coördinates of the electron in some cases become large, the velocities, however, remain in general small. Hence the magnetic field when rotating at high frequency does not impart a great velocity to the electron.

STATE UNIVERSITY OF IOWA,
November, 1921.

THE EFFECT OF AGEING ON THE SECONDARY ELECTRON EMISSION FROM COPPER SURFACES.

BY L. E. MCALLISTER.

SOME experiments on the secondary electron emission from copper surfaces were reported by Dr. I. G. Barber in the PHYSICAL REVIEW of March, 1921, and by Millikan and Barber in Proceedings of the National Academy of Science, Jan., 1921. In these reports they outline methods for obtaining measurements on the velocity of emission of secondary electrons from a copper surface and the number of secondaries emitted per primary for various velocities of impact. They also suggest a possible method for measuring the ionization potential of the surface considered. This method has been found to give consistent results to less than one volt.

Similar and modified observations on the same apparatus have been made at various times during the year following those reports. These observations show that the number of secondaries per primary as well as the ionization potential gradually increases as the surface is aged by heating in vacuo in which the residual gas is air. The number of secondaries per primary can be reduced to the original values by heating the surface in an atmosphere of hydrogen. This experiment can be done repeatedly with the same results, indicating that the copper surface gradually changes to a copper oxide surface

which can be reduced by heating in hydrogen. The copper surface was observed to be of a darker color only at the places where the secondaries were being emitted. Experiments are now in progress to test these effects on other metals.

University of Chicago.

Carbon Dioxide Band Spectra in the Near Infra-red.

By E. F. Barker.

The absorption regions of CO_2 at 2.7 μ and 4.3 μ have been reëxamined with the higher resolution afforded by a prism-grating spectrometer. The 2.7 μ region, heretofore considered to be a doublet, proves to be a pair of doublets, with centers at approximately 2.69 μ and 2.76 μ. The 4.3 μ band appears as a single doublet. Complete resolution of the band series has not been effected, but there is evidence of a "head" in each case on the side of shorter wave-lengths. The existence of this head for the 4.3 μ band is also indicated by a comparison with the emission spectrum from a bunsen flame.

From the doublet spacing an approximate value of the moment of inertia for the CO_2 molecule is obtained.

University of Michigan.

Recent Determinations of the Susceptibilities of Oxygen and Nitric Oxide and the Magneton.

By E. C. Fritts.

Pauli[1] has modified Langevin's equation for the magnetic moment of a gas per gram molecule at absolute zero. Instead of

$$\sigma_{m_0} = \sqrt{3RC_m},$$

he writes

$$\sigma_{m_0} = \sqrt{\frac{3RC_m}{\frac{1}{2}(n+1)(2n+1)}},$$

where n is a quantum number 1, 2, 3 $\cdots$. Pauli has also applied this theory to the values of the susceptibilities of oxygen and NO as determined by Piccard and found a fairly close agreement.

Piccard[2] and Soné[3] have recently redetermined the above susceptibilities. The values obtained are

Piccard,

$$\chi_{O_2} = 107.8 \times 10^{-6} \quad (20° \text{ C.}),$$

$$\chi_{NO} = 48.6 \times 10^{-6} \quad (20° \text{ C.}).$$

[1] Phys. Zeit., 21, p. 615, 1920.

[2] Jour. de Phys., Ser. VI, p. 97, 1920.

[3] Phil. Mag., 231, p. 305, 1920.

Soné,

$$\chi_{O_2} = 104.1 \times 10^{-6} \quad (20° \text{ C.}).$$

The values, for oxygen 104.1×10^{-6}, and for NO 48.6×10^{-6}, give results in still closer agreement with Pauli's equation. The ratios of the theoretical and experimental values are, for O_2 1.019, and for NO 1.067, instead of 1 where for oxygen $n = 2$ and for NO $n = 1$.

We see that oxygen at least has very nearly a magneton of Bohr with the quantum number 2, or 2 magnetons. Experiments are in progress to redetermine the susceptibilities of paramagnetic and diamagnetic gases.

UNIVERSITY OF ILLINOIS,
October, 1921.

THE GROWTH AND DECAY OF PHOTO-THERMIONIC CURRENTS FROM OXIDE-COATED FILAMENTS.

BY H. D. ARNOLD AND HERBERT E. IVES.

AN investigation of the increase of thermionic current caused by illumination. It is found that the current increment due to red light grows and decays exactly as a similar increment due to increasing the temperature of the oxide coated filament. With blue light, on the contrary, the added thermionic current grows and decays at rates different from those due to heating, and at different rates depending on the temperature. At low filament temperatures the added current rises and falls very slowly; at high temperatures it rises and falls abruptly. These properties of the added current due to blue light are considered to differentiate it from a true photo-electric current which, as far as known, rises and falls instantaneously at all temperatures. It is concluded that previously recorded observations on changes in the magnitude of the added current with variation of filament temperature, do not necessarily imply a temperature coefficient of the true photo-electric effect.

RESEARCH LABORATORIES OF THE
AMERICAN TELEPHONE & TELEGRAPH COMPANY
AND WESTERN ELECTRIC COMPANY, INC.

THE ABSOLUTE SIZES OF CERTAIN MONOVALENT AND BIVALENT IONS.[1]

BY WHEELER P. DAVEY.

IN a preceding paper[2] attention was called to the fact that if the dimensions of crystals were used alone, to find the absolute sizes of ions, the solution was indeterminate, for there were $n - 1$ equations with which to solve for n unknowns. At that time a consideration of the diffraction patterns of KCl led to the assumption that $\overset{+}{K}$, $\overset{+}{Rb}$, and $\overset{+}{Cs}$ were equal in size respectively to

[1] Abstract of a paper to be presented at the Am. Phys. Soc., November, 1921.

[2] W. P. Davey, PHYS. REV., Aug., 1921.

$\overset{-}{Cl}$, $\overset{-}{Br}$ and $\overset{-}{I}$, thus giving $n + 2$ equations for n unknowns. The concordant numerical results obtained by the use of these three additional, independent equations amply justified the assumption, at least to an accuracy of one per cent. At that time, values were reported for the "radii" of ions of the alkali metals and of the halogens. It is the purpose of the present paper to report the corresponding dimensions of $\overset{+}{Ag}$, $\overset{+}{Cu}$ and of certain bivalent ions.

Since the dimensions of bivalent metallic ions are most conveniently determined from the crystals of their oxides and sulphides, it was necessary to obtain as accurate a determination as possible of the "radius" of $\overset{--}{O}$. To this end, four routes were employed, namely (1) CsI–AgI–Ag_2O; (2) CsI–CuI–Cu_2O; (3) KCl–KF–CaF_2–CaO; (4) KCl–KF–BaF_2–BaO. The first two of these depend primarily upon the assumption that the radii of $\overset{+}{Cs}$ and $\overset{+}{I}$ are equal. The last two depend upon the assumption that the radii of $\overset{+}{K}$ and $\overset{-}{Cl}$ are equal. The last two routes are longer than the first two, so that the cumulative effect of experimental errors in the data is greater. These last routes, therefore, should not be expected to give as concordant results as the first two routes. They should, however, at least serve as valuable checks upon the validity of the results, since they are arrived at by means of values which are quite independent of those used in the first two routes.

Routes 1 and 2.—The chloride, bromide, and iodide of silver were investigated. The first two were found to be simple cubes of ions of side 2.76 and 2.89 Å. respectively. Silver iodide is a diamond-cube of ions of side 6.53 Å., *i.e.*, the shortest distance between centers of $\overset{+}{Ag}$ and $\overset{-}{I}$ is 2.83 Å. These structures are in agreement with those reported by Wilsey[1] and the dimensions agree with his to within one per cent. The chloride and bromide give "radii" for $\overset{+}{Ag}$ of 1.20 and 1.16 Å. respectively. The dimensions of the two crystals would not have to be in error by more than $\frac{2}{3}$ of one per cent. to account for this difference. The iodide gave a radius for $\overset{+}{Ag}$ of .85 Å. This discrepancy can not be accounted for on the basis of experimental error. CuCl, CuBr, and CuI crystals are all diamond-cubes of ions, with sides 2.32, 2.49 and 2.63 Å. respectively, giving "radii" for $\overset{+}{Cu}$ of .76, .76 and .65 Å. Here, as in the case of $\overset{+}{Ag}$ the values obtained from the chloride and bromide are in agreement with each other, but are larger than that obtained from the iodide. Either the silver and copper ions are of such a shape that they appear to have two dimensions (such as might be obtained by ascribing a "radius" to a tetrahedron), or they occur in two entirely different shapes, thus giving two different dimensions. The latter possibility was predicted by Langmuir[2] in the case of Ni and Pd atoms. If this possibility is granted in the case of Ni and Pd

[1] R. B. Wilsey, Phil. Mag., *42*, 262 (1921).

[2] I. Langmuir, Jour. Am. Chem. Soc., 1919.

atoms, it should also hold for not only $\overset{+}{Cu}$ and $\overset{+}{Ag}$, but also for $\overset{++}{Zn}$ and $\overset{++}{Cd}$ *ions*. It will be shown below that $\overset{++}{Cd}$ appears to have two sizes. So far, only one size has been found for $\overset{++}{Zn}$.

Ag_2O and Cu_2O were each found to consist of a body-centered cube of $\overset{--}{O}$ and a face-centered cube of the metal ion. These two cubes interpenetrate in the manner described by Bragg for Cu_2O (cuprite).[1] The sides of the cubes are 4.69 and 4.26 Å. respectively. The position of the $\overset{--}{O}$ in Ag_2O is identical with the position of the $\overset{-}{I}$ in the iodides,—it is in the center of a tetrahedron of $\overset{+}{Ag}$. The difference in "radii" between $\overset{-}{I}$ and $\overset{--}{O}$ may therefore be determined directly by the difference in the distances between $\overset{+}{Ag}$ and $\overset{-}{I}$ and between $\overset{+}{Ag}$ and $\overset{--}{O}$, *i.e.*, $\overset{-}{I} - \overset{--}{O} = 2.83 - 2.03 = .80$. Since the "radius" of $\overset{-}{I}$ is 1.98Å. the "radius" of $\overset{--}{O}$ is 1.18 Å. A similar calculation, using Cu_2O and CuI gives $\overset{-}{O} = 1.19$ Å.

Routes 3 and 4.—The structure of CaF_2 was shown by Bragg to be a modified diamond-cube. The side of this cube is 5.49 Å., so that the distance between centers of $\overset{++}{Ca}$ and $\overset{-}{F}$ is 2.38 Å. Since the "radius" of $\overset{-}{F}$ is 1.13 Å., the "radius" of Ca should be 1.25 Å. Now CaO is a simple cube of ions, of side 2.42 Å.[2] This gives a "radius" for O of 1.17 Å. BaF_2 has a structure like that of CaF_2. The side of the cube is 6.20 Å., giving a distance between centers of $\overset{++}{Ba}$ and $\overset{-}{F}$ of 2.69 Å. This gives a "radius" for $\overset{++}{Ba}$ of 1.56 Å. Bragg[3] gives the distance between centers of $\overset{++}{Ba}$ and $\overset{--}{O}$ as 2.81 Å. This leaves the "radius" of $\overset{--}{O}$ as 1.25 Å. These two values of 1.17 and 1.25, obtained by routes 3 and 4 check very well with the values of 1.18 and 1.19 obtained by the more direct routes 1 and 2. The "radius" of $\overset{--}{O}$ will therefore be considered to be 1.19 Å.

The difference in the "radii" of $\overset{--}{O}$ and $\overset{--}{S}$ as shown by BaO and BaS is .39 Å., by ZnO and ZnS, .40 Å., by CaO and CaS, .40 Å. The "radius" of $\overset{--}{S}$ may therefore be taken as 1.59 Å. The following table gives the values for the "radii" of ions which have been determined since the report in the PHYSICAL REVIEW of Aug. 1921. Crystal data on SrO and BaO are from Bragg's published work. All other data are from this laboratory.

[1] W. H. and W. L. Bragg, X-Rays and Crystal Structure.

[2] W. P. Davey, PHYS. REV., May, 1920.

[3] W. L. Bragg, Phil. Mag., Aug., 1920.

Ion.	Crystal.	"Radius."
$\overset{--}{O}$	CaO – 1.17 BaO – 1.25 Cu_2O – 1.19 Ag_2O – 1.18	1.19 – Å.
$\overset{--}{S}$	CaS – 1.59 ZnS – 1.59 BaS – 1.58	1.59
$\overset{+}{Cu}_{(1)}$	Cu Cl – .76 Cu Br – .76	.76
$\overset{+}{Cu}_{(2)}$	CuI	.65
$\overset{+}{Ag}_{(1)}$	Ag Cl – 1.20 Ag Br – 1.16	1.18
$\overset{+}{Ag}_{(2)}$	AgI	.85
$\overset{+}{Tl}$	Tl Cl	1.77
$\overset{++}{Mg}$	MgO	.90
$\overset{++}{Ca}$	CaF_2	1.25
$\overset{++}{Sr}$	SrO – 1.44 SrF_2 – 1.40	1.42
$\overset{++}{Ba}$	BaF_2	1.56
$\overset{++}{Zn}$	ZnO	.76
$\overset{++}{Cd}_{(1)}$	CdO	1.11
$\overset{+}{Cd}_{(2)}$	CdS	.95
$\overset{++}{Ni}$	NiO	.88
$\overset{++}{Sn}$	SnS	.93
$\overset{++}{Pb}$	PbS	1.33

Research Laboratory,
General Electric Co.,
Schenectady, N. Y.,
November 2, 1921.

On the Universal Distance of the Order of 10^{-8} cm. between the Centers of the Nearest Atoms in Solids.

By Albert C. Crehore.

By using the model of the atom described in previous abstracts[1] it has been found that two such atoms may unite to form a diatomic molecule. The distance between the two atoms is of the order of 10^{-8} cm., and the common

[1] Phys. Rev., April, 1921, pp. 541, 544.

angle between the line joining them and their rotation axes is about 50° 11′. So far as the translational forces are concerned the surprising result is obtained that electrostatic forces alone are sufficient to produce this stable equilibrium, that is merely by the use of the inverse square law between infinitesimal elements of charge. To obtain this result, however, requires that the ratio of the major to the minor axes of the electrons shall be about three to one. This is also the shape assigned to the electrons on other grounds in the previous abstracts cited, and, hence, the two independent results support each other.

This result is, therefore, independent of the special form of electromagnetic theory employed, whether the Saha theory or that of Lorentz. It requires between 10,000 and 100,000 such atoms strung together to bridge the distance 10^{-8} cm. This means that there is plenty of room for the smallest dimension of the molecule to be of the order of 10^{-8}, 10^{-9}, 10^{-10}, 10^{-11} or even 10^{-12} cm., and it has been difficult to understand why 10^{-8} cm. is the order selected by practically all forms of atoms as the smallest dimension of its molecules approximately speaking. The above example, which is typical of all, attributes this particular value 10^{-8} cm. to the shape of the electron itself. Granting that this is the truth of the matter, the universal presence of electrons as parts of all atoms makes it reasonable that 10^{-8} cm. should be a universal order of distance.

The secret of obtaining any result by the use of electrostatic forces so far as translational forces are concerned is connected with the kind of atom used, in which the positive and the negative electrons are already in equilibrium because of their very close proximity to each other.

CLEVELAND, OHIO,
November 7, 1921.

THE CLASSIFICATION AND THE PREDICTION OF ISOTOPES.

BY WILLIAM D. HARKINS.

AN earlier paper in this REVIEW (*15*, 73–94 (1920)) pointed out the fact that nearly all known atoms contain an even number of negative nuclear electrons. Atom nuclei may be divided into four classes. Ninety per cent. of all known atoms belong to Class I., in which the number (P) of positive electrons and the number (N) of negative nuclear electrons are both even. In Class II. N is even and P is odd and in Class III. both are odd. Almost no atoms of Class IV. exist either on earth or in the meteorites. In this class N is odd and P is even. In 1915 Harkins and Wilson developed the following equation for the atomic weights of the atomic species:

$$P = 2(M + f),$$

in which P designates the atomic weight, M is the atomic number, and f varies in steps of $\frac{1}{2}$ from -1 to 27, but for complex nuclei only from 0 to 27. The value of f gives the number of cementing electrons for all atoms whose

atomic weight is divisible by 4. The values of $2f$ are more suited for use as the basis of a system of classification, since they include only every whole number from 0 to 57, if only complex nuclei are considered. The number $2f$ may be designated as the isotopic number (n). Atoms may be classified also according to the disintegration or aggregation series to which they belong. The paper will consider a nomenclature of the radioactive and other isotopes based upon these systems of classification.

The principles previously developed indicate that in general the number of isotopes of elements of even number is considerably greater than for elements of odd atomic number, particularly for elements whose atomic number is greater than thirty. The most abundant isotope and most of the other isotopes of an element of even atomic number, have atomic weights which are even numbers, while if the atomic number is odd the atomic weights of the isotopes are almost always odd. If the chemical atomic weight is known with a high degree of precision, most of the isotopes may be predicted by the use of these and other relations.

University of Chicago.

The Nature of Charcoal "Sorption."

By H. Horton Sheldon.

It has been pointed out by Dr. J. W. McBain[1] that charcoal "sorption" of gases can be divided into two parts, adsorption on the surface and absorption into the interior. The adsorption he assumes to take place according to the theory suggested by Dr. Langmuir but the absorption he considers to be solid solution, and extends this to include the case of "sorption" of iodine from solutions of benzene, etc.[2]

Plotting the pressure-time curve for gases, or the concentration time-curve for solutions, there are evidently two distinct parts to the curve, separated by a bend. That this actually exists can be shown by plotting the logarithms of the numbers used, in which case the bend is such as to be unmistakable.

This undoubtedly means a dual action, the second beginning however only after the first is well on its way toward completion. Since solution should begin as soon as adsorption does, the bend is not accounted for and accordingly it is suggested that the second part is due to diffusion into the more inaccessible channels, which cannot be expected to take place to any extent until the easily accessible or directly exposed portions are saturated.

University of Michigan.

The Scattering of Electrons by Nickel.

By C. Davisson and C. H. Kunsman.

The emission from a nickel target under bombardment by electrons has been found to contain a small fraction of electrons with speeds comparable

[1] Phil. Mag., 6, 18, 916, 1909.

[2] Trans. Faraday Soc., XIV., 3, 202, 1919.

to the speed of the incident electrons for bombarding potentials at least to 500 volts. No certain difference has been found between the speed of the fastest of these emitted electrons and the speed of the primaries.

A study of the number of these high speed electrons emitted per unit solid angle in various directions in a plane through the incident beam shows that the distribution for bombarding potentials at least to 500 volts is characterized by two maxima. One of these lies in a direction opposite to that of the motion of the incident electrons, and the other in a direction making an angle with this that depends for its value on the bombarding potential. The maximum in the direction of the beam is not directly observed but is inferred from the form of the distribution curves in the angular range from the lateral maximum to a direction 25 degrees from the incident beam. The angle between the principal and lateral maxima is about 70 degrees for a bombarding potential of 200 volts and is greater for both higher and lower potentials.

The distribution curves are apparently unrelated to the orientation of the target except as the position of the target limits the region into which electrons are free to emerge. It is inferred from this that the complete distribution of the high-speed electrons is represented by a figure of revolution about the incident beam.

It seems reasonable to suppose that these high-speed electrons emitted from the target are primary electrons that have suffered sharp deflections without appreciable loss of energy in encounters with single nickel atoms. It is unlikely that the field about the nickel atom is sufficiently strong to reverse the direction of motion of an electron approaching it with 500 volts speed. It is equally unlikely that the encounters involve only the incident electrons and the nuclei of the atoms, as there are difficulties in this case in accounting for the more moderate deflections. It appears, however, that all of the features of the distribution curves so far observed can be reasonably accounted for on the assumption that under favorable conditions an incident electron may pass in and out of the atom structure without appreciable loss of energy, and that its deflection within the atom is determined by the field of the nucleus as modified by the surrounding shells of electrons.

If the field in and about the atom is to be reckoned on the basis of the ordinary laws of electrostatics, then the field of an atom of the Lewis-Langmuir type will be more or less similar to the field of a concentrated positive charge surrounded by concentric spherical shells of uniformly distributed negative charge—that is, the field will be, on the whole, radial, and characterized by discontinuities or, at any rate, by sharp changes through the positions of the shells. It turns out that if electrons moving with equal speeds on parallel lines are projected into such a field the scattering to be expected will have, under appropriate conditions, features similar to those exhibited by the scattering from nickel. In particular, if the system consists of a positive nucleus and a single shell of equal and opposite charge it may be shown that the intensity of scattering in a direction making an angle Ψ with the incident beam will be given by

$$I_\Psi = k\left(\frac{2\beta - 1}{(2\beta - 1)^2(1 + \cos\Psi) + (1 - \cos\Psi)}\right)^2,$$

where

$$\beta = \frac{V\rho}{E},$$

V being the potential drop through which the bombarding electrons have acquired their speed.

ρ, the radius of the shell.

and

E, the nuclear charge.

$\Psi = 0$ is the direction back along the path of the incident electrons.

An examination of this expression shows that for all values of $\beta < 1$, I_Ψ has its maximum value in the direction $\Psi = 0$. This feature is a direct result of the limitation of the field of the nucleus and is not present when the field is unlimited as in the case of the scattering of alpha particles. In this case all appreciable deflections occur inside the innermost shell of electrons. For the system equivalent to a nucleus of eight electronic charge surrounded by a shell of eight electrons and of radius 5×10^{-9} cm. $\beta = 1$ corresponds to a bombarding potential of 229 volts, so that, for such a system there should be a maximum in the intensity of scattering in the direction $\Psi = 0$ for all lower values of this potential.

The main features of the distribution curves for nickel, including the lateral maximum of variable position, are to be expected if the nickel atom has its electrons arranged in two shells. Such an arrangement is incompatible with chemical and other data which require the 28 electrons of nickel to be arranged in either three or four shells. It is not to be expected, however, that the innermost shell of two electrons will contribute any prominent feature to the distribution of scattered electrons. It is also possible that when nickel is in the solid state the outer shell of electrons is more or less completely dispersed, as has recently been suggested by Broglie and Dauvillier. On the other hand, minor details due to other shells may be found when the distribution curves are studied with greater resolving power, and other features may appear in as yet unexplored ranges of bombarding potential.

Research Laboratories of the
American Telegraph and Telephone Company,
and the Western Electric Company, Inc.,
November 4, 1921.

Width of Spectral Lines of Helium as a Function of Pressure in the Source.

By Lloyd W. Taylor.

The method of visibility-curve analysis is applied to a study of some of the more prominent lines in the visible spectrum of helium. Report is made on the width of the 5876 line as a function of pressure in the discharge tube.

Between pressures of 1 and 16 centimeters the half-width of this line is found to increase from 0.021 Å. at the lower to 0.041 Å. at the higher pressure, at a rate which is very nearly linear. This is in accordance with a law announced by Michelson in 1896.

The investigation is still under way for the purpose of measuring the width of other lines of the same gas and of extending the upper limit of pressure.

THE UNIVERSITY OF CHICAGO.

ON THE VACUUM SPARK SPECTRUM OF SILICON.

BY R. A. SAWYER AND R. F. PATON.

WAVE-LENGTH measurements on silicon have been published by Rowland, Lockyer, Exner and Haschek, Eder and Valenta, Crookes and one or two other observers. Inspection of their data shows that the various observers agree on but few lines. Even on these few lines discrepancies in wave-length occur.

Wave-lengths in the Visible Part of the Spectrum of Silicon.

Intensity.	Wave-length I.A.	Mean Wave-length by Other Observers.	Intensity.	Wave-length I.A.	Mean Wave-length by Other Observers.
1	4085.25	—	0	4673.27	—
3	4088.86	4088.86	2	4682.99	—
3	4116.16	4116.05	0	4709.03	—
3	4128.18	4128.00	3	4716.68	—
3	4131.05	4130.99	1	4733.35	—
1	4150.26	—	1	4800.37	—
0	4153.25	—	2	4813.21	4812
1	4190.96	4190.0	2	4819.54	4819
1	4198.25	4198.0	3	4828.81	4829
1	4212.64	—	0	4907.23	—
1	4215.58	—	0	4922.28	—
0	4254.42	—	0	4933.97	—
0	4257.66	—	3	5041.28	5043.2 ± 1.5
0	4259.21	—	4	5055.96	5058.0 ± 1.5
0	4262.29	—	0	5182.32	—
1	4267.19	—	0	5186.36	—
1	4277.91	—	0	5192.66	—
0	4314.26	—	1	5202.98	—
1	4328.31	—	0	5669.8	—
2	4338.54	—	0	5689.9	—
10	4552.52	4552.57 ± .25	2	5740.2	5740.4
8	4767.59	4767.65 ± .5	0	5868.4	—
7	4574.67	4574.64 ± .2	0	5889.7	—
1	4619.45	—	1	5957.8	5960.6 ± .8
2	4631.15	—	1	5979.4	5980.3 ± 1.5
1	4638.23	—	2	6347.9	6346.8
2	4654.07	—	1	6372.2	6370.1 ± .7
1	4665.54	—			

The difficulties which these observers have met have been largely experimental. Due to the rapid oxidization of silicon in the spark satisfactory spectra have been very difficult to obtain. It seemed to the writers that the vacuum spark, developed by R. A. Millikan and one of the writers, should overcome this difficulty. For in the vacuum spark we have a means of producing a high voltage spark of great energy and with no possibility of oxidization.

A brass box was built which could be evacuated to an extremely low pressure by mercury vapor pumps. In this box silicon electrodes were mounted and the vacuum spark produced somewhat after the manner described by one of us (Astro. J., II., 286, 1920). Through a window in the box the spectrum of these sparks was photographed with a prism spectrograph. An iron arc comparison was used to determine the wave-lengths. The following table contains the wave-lengths in these spectra which are probably due to silicon. The wave-lengths due to impurities, which are chiefly iron, aluminum and calcium have been eliminated. It is believed that these wave-lengths are accurate in the range from 4100–5202 to one tenth of an Ångstrom or better, in the range from 5600–6400 to about three tenths of an Ångstrom.

Among these lines several groups of pairs of constant frequency difference have been noticed. The three most numerous groups of such pairs are included in the following table.

Pairs of Constant Frequency Difference in the Silicon Spectrum.

Int.	Wave-length	Fre-quency.	*dn.*	Int.	Wave-length.	Fre-quency	*dn.*	Int.	Wave-length.	Fre-quency	*dn.*
0	4907.23	20378.1	62.3	3	4128.18	24224.3	17.4	8	4567.59	21893.4	33.9
0	4922.28	20315.8		3	4131.05	24206.9		7	4574.67	21869.5	
0	5186.36	19281.4	61.6	1	4150.26	24094.9	17.4	2	4631.15	21592.9	33.0
1	5202.98	19219.8		1	4153.25	24077.5		1	4638.23	21559.9	
0	5669.8	17637.3	62.3	1	4212.64	23738.1	16.6	1	4665.54	21433.8	35.5
0	5689.7	17575.0		1	4215.58	23721.5		0	4673.27	21398.3	
0	5868.4	17040.4	61.6	0	4254.42	23505.0	17.9	0	4709.03	21235.8	34.4
0	5889.7	16978.8		0	4257.66	23487.1		3	4716.68	21201.4	
1	5957.8	16784.7	60.6	0	4259.21	23478.5	16.9				
1	5979.4	16724.1		0	4262.29	23461.6					
2	6347.9	15753.2	60.0								
2	6372.2	15693.2									

University of Michigan.

The Sparking Potential in Argon at Reduced Pressures.

By E. R. Stoekle.

In the course of some experiments with an arc between calcium electrodes in a pressure of 40 mm. of argon, it was found that the potential required to start an arc decreased to unexpectedly low values after the arc had been allowed to run for some time. For example, such a discharge tube filled with argon purified in an auxiliary calcium arc discharge, would require a starting potential of 300 volts shortly after being sealed from the line, but after being run at 3 amperes for about an hour, and then being allowed to cool, it restarted at only 108 volts. After running for several hours at this current, the arc could be cooled and restarted at a potential of only 90 volts. Even after standing cold for 15 hours the arc could be restarted at 120 volts. These values of the potential required to start a discharge in argon are far below the minimum sparking potential of 240 volts given for argon by Townsend.[1]

The most probable explanation of these low sparking potentials lies in the progressive purification of the argon by the calcium vapor formed in the arc discharge. There is, however, a probability that some slow chemical action between the calcium electrode and a trace of oxygen or other gas might cause the emission of electrons after the manner described by Haber and Just, and thus facilitate the starting of a discharge. In order to avoid such an effect, the sparking potential between brass electrodes in argon purified by a calcium discharge was studied.

The apparatus consisted of a discharge tube containing two circular brass electrodes of 35.5 mm. diameter, whose opposing faces were spherical surfaces of 10 cm. radii of curvature, and distant 3.20 mm. at their nearest points.

Two calcium electrodes were mounted in the same tube for the purpose of purifying the argon. The tube was connected to a mercury vapor pump and a supply of argon, and could be shut off from both lines by means of a mercury valve. After being thus shut off the pressure in the tube could be varied over a range of about 50 per cent. by means of an attached bulb, whose volume could be changed by adjusting the level of the mercury within it. A McLeod gauge reading up to 2.5 mm. pressure and a manometer for reading the higher pressures were attached to the tube.

In order to get rid of adsorbed gases in the apparatus, it was baked at 360° C. for three hours and the electrodes were heated by passing a discharge between them in argon, which was pumped out while the discharge was going on. Argon which had been purified by exposing it to a calcium arc discharge for a period of 10 hours and dried by passing it through a trap surrounded by carbon dioxide snow was then admitted to the apparatus. The calcium arc in the discharge tube itself served for the final purification, and this was performed after the tube had been shut from the line.

The sparking potential was observed by slowly raising the voltage between the electrodes by increasing the field excitation of a 500-volt generator. A

[1] Electricity in Gases (1915), p. 329.

resistance of 3,000 ohms was placed in series with the electrode gap, in order to limit the current and as soon as the discharge passed the circuit was opened to prevent unnecessary heating of the electrodes, which might cause the evolution of electrode gases. For each observation three readings were taken, about four minutes apart, and in general these agreed to within 3 per cent. All observations were taken in rather dim diffused daylight and no special means for initiating ionization was provided.

A minimum sparking potential of 176 v. for this relatively impure argon was found to occur at a value of $p \times d = 8$, when p is the pressure in millimeters of mercury and d is the distance between the electrodes in millimeters. For the argon purified by the calcium arc in the discharge vessel a minimum sparking potential of 137 volts occurred at $p \times d = 7$.

The values of sparking potential obtained in this apparatus, although lower than any known to the writer, may not be as low as could be obtained in still purer argon. The slightest trace of impurity, such as an air bubble liberated from the mercury in the gauges or in the mercury valve would produce a marked change in sparking potential with no observable change in the pressure. A series of such bubbles, which were allowed to enter the apparatus, changed the pressure about 1 per cent., but changed the sparking potential by 7.5 per cent. It is, therefore, thought that by devising special means for measuring and varying the pressure of the argon without introducing impurities a lower minimum sparking potential than the observed 137 volts may be found to exist.

Physical Laboratory,
The Cutler-Hammer Mfg. Co.

"The Action of Light on a Photographic Film."

By Jay W. Woodrow.

It is a well-known fact that there is a remarkable similarity between the photoelectric and photographic properties of the silver halides. This has suggested to several writers (cf. Allen's "Photoelectricity," Chap. XIV.) the possibility of explaining the action of light on the photographic film as due to some sort of photoelectric action.

Now it has been shown that when plane-polarized light is incident upon a photoelectrically sensitive surface, more electrons are emitted when the electric vibration in the incident light is normal to the surface than when it is parallel to it. Consequently a very narrow line if photographed through a Nicol's prism should appear sharper when the direction of the electric vibration is parallel to the line than when at right angles to it. This was tried experimentally and found to be the case.

The source of light consisted of a very carefully ruled set of rectangular lines on a plane white background. Between this source and the camera lens was a high-grade Nicol's prism. The lens was a good anastigmatic lens, and fine-grained, contrast photographic plates were used.

Several photographs were taken with the Nicol so oriented as to make the

electric vibration parallel to the vertical lines and several with it parallel to the horizontal lines. In every case the lines parallel to the electric vector were the sharper. The direct image on the ground-glass of the camera was also examined with a magnifying glass but no difference could be observed between the two sets of lines.

These experiments seem to indicate the possibility of explaining the effect on the assumption of some photoelectric action. The experiments are being continued in a slightly different manner with the object of finding some more direct evidence of the effect.

IOWA STATE COLLEGE,
AMES, IOWA.

THE INSTRUCTIONAL VALUE OF CERTAIN TYPES OF MOTION PICTURES.

BY HARVEY B. LEMON.

THE motion picture possesses certain obvious advantages over the spoken lecture in technical instruction. By means of animated drawings certain types of small and rather complex mechanisms may be made clearer than by any other means. Experiments performed by means of photography on the screen never fail to function and may be repeated indefinitely. Motions much too rapid for the eye to follow may be slowed down and analyzed. These facts are universally recognized.

A direct comparison has been made at this laboratory of the relative effectiveness of the spoken demonstration lecture and the presentation of the same material by means of films. Classical experiments in electricity and magnetism were set up and photographed. The films were assembled with suitable explanatory titles and drawings and projected before a large class. The class was then given an examination covering the material presented. Another class received the lecture in the conventional fashion with the experiments themselves presented on the table. They were given the same examination as the others. The classes were interchanged. Other material was presented to both, but conditions were now reversed and those who formerly saw experiments now saw pictures of them, and vice versa. Each group was checked by examination. Examinations were graded by four different men all familiar with, and teaching in, the fields covered. Sufficient numbers of students were involved to ensure statistical results.

The final results gave confidence in the effectiveness of the film. Grades obtained from the motion picture presentation ran about 67 per cent.—those from the spoken lectures about 72 per cent. Other facts made this difference less significant.

The film was unsupported by any comment either before, during or after the showing. It occupied 15 to 20 minutes time: the spoken lecture, 60 minutes. The experiments themselves required two to three hours of labor in the preparation. The film, once obtained, required none.

It must be borne in mind that the above described work makes comparison

between films and but one of many types of instruction,—the demonstration lecture. Comparisons of films with laboratory methods, recitations, or problem solving types of instruction which are the *most important* teaching methods in science, would be obviously absurd.

University of Chicago,
November 9, 1921.

Sensibility of the Ear to Small Differences in Intensity and Frequency.

By V. O. Knudsen.

A telephone receiver energized by a current from a vacuum tube oscillator is used as a source of sound for determining the sensibility of the ear to small differences of loudness and pitch. Tones varying in frequency from 30 d.v. to 20,000 d.v. are produced by the oscillator used in these experiments. By means of a divided resistance circuit the intensities of the tones can be varied by any desirable and measurable intervals from the threshold values up to very high values.

Some auxiliary experiments showed that the acoustical energy developed by the receiver diaphragm is a linear function of the electrical energy which actuates it. The electrical energy is therefore a convenient measure of the relative acoustical energy at any fixed frequency.

Data that have been taken thus far on a limited number of ears show that the sensibility of the ear to small differences in intensity, measured by the ratio of the smallest perceptible increment in energy to the whole energy, $\Delta E/E$, is —.

1. Dependent upon the intensity. The ratio $\Delta E/E$ decreases as the intensity increases. For a wide range of moderate and high intensities the sensibility is nearly constant. Its value for ordinary frequencies is roughly 0.10.

2. Nearly independent of the frequency between 100 d.v. and 4,000 d.v.

3. Nearly the same for all normal ears.

The sensibility of the ear to small differences in frequency measured by the ratio of the smallest perceptible increment to the whole, is —

1. Dependent upon the intensity. The law of variation with intensity closely resembles the law of variation of sensibility to small intensity differences.

2. Dependent upon the frequency. The sensibility ratio decreases from about 0.01 at 50 d.v. to about 0.002 at 1,000 d.v. For higher frequencies the ratio increases.

3. Only approximately the same for different ears.

University of Chicago.

The Efficiency of Artificial Aids to Hearing.

By Paul E. Sabine.

Measurements were made to determine the amplification of sound by eleven different instruments commonly employed for the aid of the deaf. The measurements were made by timing the duration of sound, after the source of sound had ceased in a sound chamber, audible to a deaf person, with and without the instrument held to the ear. From the difference of time with and without the instrument and the known rate of decrease of intensity as the sound dies away in the room, the ratio of the intensities at the ear of the observer under the two conditions was computed by the equation

$$\log_e \frac{I_1}{I_2} = A(t_1 - t_2).$$

A being defined by the equation

$$\frac{dI}{dt} = -AI.$$

The experiments covered the range of pitch from 128 to 4096 d.v.

The amplifications produced by different instruments of the trumpet type were found to follow order of size of these instruments. The effect of the natural frequencies of the air columns enclosed by the trumpets were shown by increased amplifications for these frequencies. Instruments in which the vibrations of diaphragms held in contact with the teeth are supposed to be conducted to the auditory nerve by the bones of the skull were found to produce positive, though small amplifications. Telephonic devices showed relatively large amplifications for tones in the neighborhood of the natural frequencies of the diaphragms of the transmitter and receiver.

By comparison with the duration of sound audible to normal ears, the sensitivity of the ears of the deaf observer was determined in terms of norma sensitivity. The ratio of sensitivities so determined was of the order of 10^5 in the middle register. The maximum amplification produced by any of the trumpets was approximately $10^{1.3}$, while that for the telephone at the natural frequency of the receiver was $10^{2.5}$. The inadequacy of any of the instruments tested in the relief of cases of extreme deafness is thus shown.

Wallace Clement Sabine Laboratory,
Riverbank, Geneva, Ill.

Doppler's Principle Illustrated by Ripple Waves.

By F. R. Watson and W. B. Worsham.

The Doppler effect was observed when a source of ripple waves on water was made to move. The waves were generated by a jet of air directed against the surface of the water. For some cases, the stream of air was made to come in periodic puffs and the resulting waves were observed by means of a stroboscopic device so that they appeared to move slowly.[1]

[1] "A Study of Ripple Wave Motion," Phys. Rev., Vol. 7, pp. 226–228, 1916.

When the velocity of the source was less than the velocity of propagation of the waves, the waves were crowded together in front of the moving source thus giving an increase in the frequency, whereas behind the source, the waves were spread out corresponding to a fall in pitch. If the source was moved more rapidly than the waves, an overlapping resulted so that a tangent drawn to the contiguous crests gave a resultant similar to the wave set up by a bullet in flight.

Photographs were taken of a number of type cases with (1) the velocity of the source less than the wave velocity, (2) the velocity of the source greater than the waves, (3) the velocity of the source approximately equal to that of the waves, (4) various intermediate conditions.

Since these waves appear to move slowly, data may be obtained with comparative ease and thus yield information that will assist in explaining the phenomena of bullets in flight as well as other examples of Doppler's principle.

By photographing a scale with the waves, the wave-length may be found, so that, if the frequency of the puffs of air is known, the velocity of the source v may be calculated. By measuring the angle θ, between the median line and the wave front, the velocity V of the waves may be found according to the formula

$$V/v = \text{Sin}\ \theta.$$

University of Illinois,
October, 1921.

Einstein's Relativity and Gravitation.

By John Millis.

Note is made of certain errors and misapprehensions found in publications relating to the relativity theories as indicated by the recently published book "Einstein's Theories of Relativity and Gravitation" by J. Malcolm Bird, associate editor, Scientific American. Considerable lack of clearness is found as to the real purpose and significance of the famous Michelson-Morley experiment. This, in a few words, was undertaken to test the relative movement of the apparatus used and the supposed medium which transmits light, the ether. No such relative movement has ever been detected either by this or by a number of other similar tests that have been carried out. The Lorentz-Fitzgerald explanation of this failure which is that the dimensions of all matter are affected by motions relative to the ether and that therefore no such relative movement can ever be detected by man, is not only highly improbable but is fallacious in the assumption that an ether could exist without its being possible to detect its presence by similar tests. It is shown that if an ether does exist and that if it affects matter as assumed, an apparatus could be constructed that would reverse this effect and therefore disclose it.

Some writers appear to assume that there is some relation between the so-called Lorentz-Fitzgerald effect in connection with the ether and the discrepancies that arise in certain measurements because of the time required to

convey intelligence from sensible distances. The velocity of light appears in both, but there is no real connection between them; the first is a mere speculation while the second is a reality.

It is demonstrated that there cannot be any superior limit to possible relative velocities; in other words, that the velocity of light is not such a limit, as has been assumed. The assumption that there can be a change of mass with change of velocity is also fallacious. Since all velocity is relative and a body may have an indefinite number of velocities at the same time, this assumption of a relation between mass and velocity would require that a body could have an indefinite number of masses simultaneously. Energy has been regarded as something definite or fixed, but a body may have an indefinite number of energies at the same time, depending on relative velocity.

There can be no special significance in the velocity of light as such as a fundamental physical principle. Such an assumption would be attaching to one of the sense organs of human beings who have had a comparatively recent career in the universe, an importance in connection with a general physical theory that facts do not warrant.

It is shown that certain ideas connected with centrifugal force in a relative sense are erroneous and it is also pointed out that the celebrated Foucault pendulum experiment and the behavior of the gyroscope do not establish the persistence of motion of a body "in space." These only show a tendency to preserve motion or position respecting the axis of the earth. Reference is made to the "Shadow-bands" which have been observed during a total eclipse near the edge of the moon's shadow as it passes over the earth and it is suggested that there may be some relation between the cause of these bands, whatever it is, and the displacement of stars observed during a total eclipse which has been regarded as confirming the Einstein theories.

The non-existence of any universal medium like ether is more comprehensible and consistent with the general structure of nature than would be such a medium as a demonstrated fact—this, notwithstanding the difficulty of understanding how gravitation and other so-called forces can be transmitted without any medium.

542 RUSH ST., CHICAGO, ILL.

SOME ASPECTS OF THE THEORY OF RELATIVITY.

BY A. C. LUNN.

THE Einstein theory may be considered as based on a combined differential geometry of space and time measurements but amplified into a comprehensive physical theory by the addition of various notions and postulates consistently interpretable in connection with the geometry but at least not known to be definable or deducible from it. Since particular contacts with experiment are concerned with these additional assumptions as well as with the main geometric basis it is conceivable that adaptation to results of observation may require,

and be attainable by, changes in some of these without departure from the general program.

This paper surveys the geometric materials available for physical interpretation, the extent to which physical theory has so far been absorbed into that interpretation or superposed upon it. At several points it appears that there is some flexibility of choice possible in certain of these auxiliary postulates, in particular as concerned with the relation of optical and mechanical phenomena within material bodies, the phenomena of rotation, and the meaning of an electromagnetic field.

University of Chicago.

Atomic Constants and Dimensional Invariants.

By A. C. Lunn.

It has been recognized for some time that the number of universal physical quantities revealed by experiment, but not yet utilized for the practical reduction of the system of arbitrary units, is more than sufficient to complete that reduction so as to give for every kind of measurement a natural unit. Since in most cases the measurements are not yet accurate enough for putting this reduction into effect it is convenient to retain consideration of those quantities as having dimensions corresponding to the scheme of units antecedent to such reduction. The redundancy means then that the excess quantities should be expressible in terms of the others, and several relations of this kind have been proposed. Equivalently, there must exist a number of dimensional invariants corresponding to this excess. On the one hand the recomputation of a suitable list of such invariants gives an impartial scheme for introducing improved values from measurement, and on the other a test of the scope of theory in a certain sense is found in the number of invariants whose values as deduced accord with experiment.

As illustration this paper lists seven quantities which can be considered as dimensioned in the familiar three-unit scheme and hence must have a fundamental system of four invariants, to which may be added the mass ratios of hydrogen and helium atoms to electron. The theories of Planck, Bohr, and Lewis and Adams in effect assign numerical values to three of these, and in this paper are shown certain tentative values for others enough to complete the list, so accurate in terms of present data as to suggest the possibility of deduction from theory, and such as to give in particular simple formulas for the action constant and constant of gravitation.

University of Chicago.

Measurements of the Amount of Scattered Homogeneous X-rays of Wave-length 0.712 Å. per Gram of Carbon.

By C. W. Hewlett.

A narrow beam of x-rays from a molybdenum Coolidge tube excited at 30 k.v. was first passed through a zirconium filter and then allowed to fall on

the scattering material. The radiation transmitted by the filter under this condition was nearly homogeneous, being almost entirely the α_1 radiation of the K series of molybdenum.

The scattering material was contained in a cylindrical capsule 0.47 cm. in diameter and was mounted on the axis of an x-ray spectrometer in such a way that it could be continuously rotated during the scattering measurements. The scattered radiation was received by an ionization chamber which was mounted to rotate about the spectrometer axis and about 36 cm. from the scattering material. The ionization current was measured by a quadrant electrometer. The width of the primary beam of x-rays was slightly greater than that of the capsule of scattering material, and its height was 2.40 cm.

The scattering of powdered artificial graphite, liquid mesitylene and diamond chips was measured between 2° and 158° from the incident beam. The amount of scattering material for graphite and mesitylene was about 0.35 gm., and for diamond about 0.79 gm.

The intensity of the incident beam and that of the scattered radiation was measured in the same units. The total absorption coefficient, and the total amount of radiation taken from the primary beam by the scattering material, was measured for graphite and mesitylene. The total scattered radiation was then calculated as a fraction of the total radiation taken from the primary beam, making an estimated allowance for the scattering in the 0.50 unit solid angle inaccessible to the ionization chamber, and for the absorption of the scattered radiation within the scattering material. It was assumed that the true mass absorption coefficient of diamond was the same as that determined for graphite and mesitylene and the mass scattering coefficients of all three were calculated with the following results:

Substance.	Density	True Mass Abs. Coeff.	Mass Scattering Coefficient.
Mesitylene	.863	.351	.184
Graphite	1.48	.351	.198
Diamond	3.51	.351	.234

The above results are probably not in error by as much as 10 per cent.

Thomson's theory of scattering gives for carbon a mass scattering coefficient of .200. This is based on the assumptions (*a*) that the electrons are small compared to the wave-length of the primary beam, and (*b*) that they scatter independently. This latter condition is very probably not satisfied in the scattering by carbon of wave-length 0.712 Å. The increase in the scattering coefficient with increasing density shown in the accompanying table is very probably due to the fact that as the atoms get closer together the electrons under the influence of the primary radiation vibrate more nearly in phase and consequently emit more scattered radiation.

The distribution of the scattering for graphite and diamond shows the maxima characteristic of the crystal structures of these materials. The actual

amount of scattered radiation in the lines is however only a small per cent. of the total scattered radiation, a large part of it lying in between the maxima. Theory predicts a large intensity of scattering at very small angles from the primary beam, but these experiments show that the scattering approaches zero at these small angles. Determinations of the absorption coefficient in aluminum of the scattered radiation at fourteen angles about equally distributed in the region of investigation failed to show any difference in quality of the scattered and primary radiation.

State University of Iowa,
Iowa City, Iowa.

The Spectrum of Secondary X-rays.

By Arthur H. Compton.

An examination of the secondary rays excited in different materials when x-rays rendered nearly homogeneous by filtering were employed, showed that the secondary radiation was of a softer type than the primary rays which struck the radiator.[1] More recent experiments have shown that this phenomenon is not confined to heterogeneous x-rays, but occurs also when the rays incident upon the radiator have been reflected from a crystal.[2] The most obvious interpretation of these results was that in addition to scattered radiation there appeared in the secondary rays a type of fluorescent radiation, whose wave-length was nearly independent of the substance used as radiator, depending only upon the wave-length of the incident rays and the angle at which the secondary rays were examined.

In order to obtain more definite information with regard to the characteristics of the secondary x-radiation, a study has been made of the spectrum of the secondary rays excited in various substances by the x-rays from a Coolidge tube having a molybdenum target. A small piece of radiating material, such as celluloid or aluminium, placed in front of the first slit of the spectrometer, was illuminated by incident x-rays at approximately 90° with the secondary beam under investigation. The spectrum was studied by means of a calcite crystal grating, using both the ionization and photographic methods.

The spectra obtained show lines identical in wave-length with the primary K lines from molybdenum, thus proving that a part of the secondary radiation is truly scattered and unchanged in wave-length. In addition to these lines, a general radiation is observed which is more prominent in the secondary than in the primary beam. When the x-rays incident upon the radiator were unfiltered, the general secondary radiation had a broad intensity maximum at a wave-length slightly under 1 Å. U. On introducing a zirconium filter between the x-ray tube and the radiator, thus giving a primary beam consisting principally of the $K\alpha$ line from molybdenum together with some fluorescent K rays from zirconium, a much sharper maximum in the secondary fluorescent

[1] Phys. Rev., 18, 96 (1921).

[2] Nature, Nov. 17, 1921.

radiation was observed. This result has been verified by means of photographic spectra, which show a maximum of the general radiation at about 0.95 Å.U., which is about 35 per cent. greater than the wave-length of the exciting ray.

The energy in this general radiation is roughly 30 per cent. as great as the energy of the scattered K rays. Previous experiments have shown that when shorter wave-lengths are employed, the energy in the fluorescent rays may be even more prominent than the truly scattered rays. If we suppose that the incident x-ray beam ejects electrons moving forward with a kinetic energy hC/λ, where λ is the wave-length of the exciting ray, and if the ejected electron is oscillating at such a frequency that as observed in the direction of motion the wave-length is λ, on account of the Doppler effect the wave-length of the radiation at right angles with the primary beam will be very close to that of the fluorescent rays observed in these experiments.

WASHINGTON UNIVERSITY,
SAINT LOUIS.

OSCILLATIONS OF TEMPERATURE OF AN INCANDESCENT FILAMENT, AND THE SPECIFIC HEAT OF TUNGSTEN.

BY K. K. SMITH AND P. W. BIGLER.

THE primary object of this experiment was to test the practicability of using thermionic currents to record rapid changes in the temperature of a filament. By means of a double high-frequency oscillograph we have obtained continuous photographic records showing simultaneously the cyclic variations in thermionic emission from an incandescent tungsten filament in vacuo, and the variations in the alternating voltage across the filament. The thermionic current is a direct current on which are superposed oscillations of twice the supply frequency, which is 60 cycles per second. The constant potential difference, 220 volts, between the filament and the cylindrical anode was more than sufficient to secure saturation, and consequently variations in the thermionic current were produced wholly by changes in temperature. The thermionic current was returned through one strip of the oscillograph to the middle of a high resistance, and thence to the two ends of the filament so that the disturbing effect of the thermionic current was negligibly small. The other strip of the oscillograph was in series with a voltmeter, and this strip and the voltmeter formed a second shunt across the filament.

From observations on the change in the mean thermionic current resulting from a known change in the mean temperature, the measured variations on the plates have been translated into oscillations of temperature above and below the mean value. The lag of temperature behind the power has been found on the assumption that the thermionic emission is in phase with the temperature.

The theoretical relation between the oscillation in temperature and the heat capacity of the filament was deduced by Corbino[1]

[1] Phys. Zeitschr., XI., pp. 413–7, 1910.

Writing c = mean heat capacity of the wire in joules per degree,
$e_0 \sin \omega t$ = voltage between the ends of the filament,
T = instantaneous temperature,
$f(T)$ = total rate of loss of energy from the wire,
a = temperature coefficient of resistance,
r_m = resistance at mean temperature T_m,
θ = variation in temperature from T_m.

he has, from the energy principle,

$$c\frac{dT}{dt} + f(T) = \frac{e_0^2 \sin^2 \omega t}{r_m(1 + a\theta)}.$$

When θ is small in comparison with T_m, and Q is written in place of $a \cdot f(T_m) + df(T)/dT$, the differential equation reduces to

$$c\frac{d\theta}{dt} + Q \cdot \theta = -f(T_m) \cos 2\omega t.$$

The solution of this equation can be expressed in the form

$$\theta = \Theta \cdot \cos (2\omega t - \phi),$$

where Θ = the amplitude of the oscillation of temperature $= [-f(T_m) \cos \phi]/Q$, and $\tan \phi = 2c\omega/Q$.

Eliminating Q between the last two equations, and replacing $f(T_m)$ by W, the mean power spent in the wire, Corbino expressed the heat capacity in the form $c = -(W \sin \phi)/(2\omega\Theta)$.

The mean temperature of the filament was calculated from Langmuir's data on the volt-ampere characteristics of tungsten.[1] The filament, 0.004 cm. in diameter and 14.25 cm. long, was mounted along the axis of a pyrex tube 2.5 cm. in diameter, which contained a concentric cylinder of copper gauze 2.28 cm. in diameter. The evacuated lamp was heated in a furnace for a number of hours to free it from gases, and a very high vacuum was maintained while the experiments were performed.

The results for the plates on which measurements have been completed are as follows:

Plate.	Mean Temp. T_m.	Watts W.	Θ °	ϕ °	Spec. Heat $S = \frac{c}{(\text{mass of filament}) \times 4.18}$
1	2485 K.	13.75	28.5 K.	(91.5)	.0450
2	2455	12.99	24.5	86.4	.0495
3	2435	12.49	24.5	87.1	.0477
4	2413	11.91	22.6	86.8	.0491
5	2368	11.03	21.2	86.1	.0485

Mean value of specific heat $= .0479 \frac{\text{calories}}{\text{gm. degree}}$.

[1] Physical Review, VII., pp. 315–6, 1916.

Hence the atomic heat at constant pressure is 8.75 calories per gm. atom per degree. This agrees within the limits of experimental error with the results which Worthing[1] obtained by observing the way in which the resistance of a tungsten filament varied when the heating current was suddenly changed.

An attempt is being made in this laboratory to increase the accuracy of the oscillographic method, and to apply it to the determination of the specific heats of other metals.

An oscillograph might also be used to record the variation in temperature of a filament when a direct current is varied.

NORTHWESTERN UNIVERSITY,
November 7, 1921.

EFFECT OF TENSION ON THERMOELECTROMOTIVE FORCES BY MAGNETIZATION.

BY ALPHEUS W. SMITH.

THE application of tension to nickel at first lessens the change in resistance, length and thermoelectromotive force produced by a longitudinal magnetic field. For larger magnetic fields the reverse is true. In the case of nickel there is a proportionality between the change of length, resistance and thermoelectromotive force. In iron there is a parallelism between the effect of tension on the change of length and change of thermoelectromotive force. The greater the tension, the smaller the initial increase in the thermoelectromotive force and the smaller the magnetic field at which the reversal of the direction of the change takes place. At sufficiently large values of the magnetic field the initial increase in the thermoelectromotive force disappears and there is a decrease for all values of the magnetic field.

The variation of thermoelectromotive forces in iron-copper alloys is very similar to its variation in pure iron. The addition of copper to iron at first increases the fractional change of the thermoelectromotive force. When the alloy contains about 1.5 per cent. copper this fractional change is largest. Beyond this concentration there is a decrease. In these alloys there is a similarity between the Hall constant, the specific resistance and the fractional change of thermoelectromotive force. The first addition of nickel produces an increase in the fractional change of thermoelectromotive force. This is followed by a decrease and a later reversal both in the direction of the thermoelectromotive force and in the sign of its change.

Neither the gas-free theory of electric conduction and thermoelectromotive force nor the gap theory of Bridgman give satisfactory explanations of the effect of longitudinal magnetic fields on thermoelectromotive forces, length and resistance and their variation with tension. The assumption that the number of free electrons is determined by the frequency of the atom and that this number decreases with increasing frequency would lead naturally to the conclusion that an elongation would produce a decrease in frequency, an increase in the number of free electrons and a decrease in resistance. Where

[1] PHYS. REV., XII., p. 216, 1918.

the frequency of the atom and the number of free electrons are not the same functions of the magnetic field at different temperatures and tensions this form of explanation might give a reason for the variation of the thermoelectromotive force and for the influence of tension on it.

Ohio State University.

Positive Ray Analysis of Lithium and Zinc.

By A. J. Dempster.

Positively charged atoms are formed by vaporizing the metal in an electrically heated capsule, and bombarding the vapor with electrons from a hot cathode. After falling through a definite potential the particles are deflected through 180° by a magnetic field, the semicircular path being smaller for the lighter than for the heavier. The different atoms are observed by means of their charge. Two components were observed in the case of lithium with atomic weights 6 and 7. The proportion of the two components was found to vary in different experiments. Preliminary experiments with zinc have given three strong components two units apart in atomic weight, and one weaker component one on the heavy side of the strong group and separated also by two units of atomic weight.

Ryerson Laboratory,
University of Chicago.

A Convenient Contactor for Small Currents.

By Frederick J. Schlink.

Ordinary drawing ink applied in the form of lines with a ruling pen will form an electrical path of sufficient conductivity to be used in connection with the oscillograph for recording the instants at which the lines pass by a brush or wiper. As it is frequently necessary to determine electrically the rate of translation or rotation of some moving part, the possibility of providing for the electrical contacts required by simply drawing lines on a strip of paper gummed to the moving part, affords great convenience, in comparison with the trouble and expense of constructing the usual composite commutator for the purpose. Moreover, the ink and paper contacting device will often be of negligible mass and inertia in relation to the part whose motion is under investigation. The lines may be connected to a common return circuit by drawing transversely across them a wide band of the same material, which in turn may be connected to a metallic return path through wire, metallic foil, or similar connection.

The contact pressures required will be extremely minute, and as the ink and paper are sensibly in the same plane, difficulty from bouncing of the brush will not be encountered unless the velocities are very high indeed. It is found that the drawing ink will carry a considerable amount of graphite in suspension; addition of this will increase the conductivity markedly, especially if the ink after drying be burnished and compacted to a glossy condition by the use of a smooth metallic tool.

It is found that in practice, if every fifth or tenth line is emphasized by being drawn somewhat wider than the others, the effect will be recorded in the oscillogram by the greater amplitude corresponding to the higher conductivity of the wider line. In exceptional cases, where, in order to obtain a high precision or "definition" of the contact, a very narrow line must be used, of correspondingly low conductivity, a d.c. amplifier introduced into the circuit will enable sufficient amplitudes to be obtained in the usual G.E. oscillograph.

There seems to be a fair possibility of obtaining a space-time curve direct by the use of a brush passing along, instead of transversely to such an ink line, in which case resistance would be cut in or out proportionally to the relative displacements of the brush and the line, but opportunity has not been available to try out this method. Undoubtedly a variable resistance of this character would not be constant in its value; this would not, however, be a matter of serious moment if the method were required only for occasional use, as a preparatory calibration could readily be made.

WESTERN ELECTRIC CO.,
NEW YORK,
May 27, 1921.

THE DIELECTRIC CONSTANT OF MICA.

BY J. R. WEEKS, JR.

IN looking for an average value of the dielectric constant of mica, the writer was impressed with the wide variations, 2.5 to 10, found by different investigators. It seemed likely that at least a part of this large variation might be due to air pockets or films between the various laminæ, especially since most of these low values were found on rather thick sheets. The high values, on the other hand, might be due to conducting films between the laminæ increasing the effective area of the electrodes.

Accordingly the dielectric constant of 12 different grades of mica was determined, using a shielded capacity and conductance bridge to measure the capacity of a condenser formed by two mercury electrodes and the sheet of mica. These 12 grades included some of those for which other investigators found abnormally high or low values.

It was found that:

1. When air films in the interior of the sample of mica were eliminated by splitting it along its natural lines of cleavage into thin sheets, in no case was the dielectric constant less than 6.4.

2. Where air films were plainly visible, the dielectric constant was low (2.9 to 4.8).

3. The most probable cause of very low values as found by some investigators is the existence of air films between the laminæ. These air films are in most cases very hard to see without carefully examining the edges of the sheets.

4. Stained sheets did not show a dielectric constant enough higher than the average value of 8.1 to determine the effect of stains in mica upon the dielectric constant.

5. No difference in the dielectric constant is readily discernible between the different grades or kinds of mica which were tested.

Research Laboratories of the
American Telephone and Telegraph Company
and Western Electric Company, Inc.

A Photomicrographic Study of a Series of Drawn Tungsten Wires.

By L. P. Sieg.

The writer has reported[1] on the effect of drawing on the coefficient of simple rigidity of ductile tungsten wires. These wires, five in number, were all drawn down from the same original wire, and so, presumably, had the same chemical constitution. Their rigidities were found to increase progressively with decrease in diameter. In the above published reports the hypothesis was advanced that if the drawing produced a surface effect, penetrating to a moderate distance, and if this surface state of the wire possessed the higher rigidity, then the results could be accounted for. It remained to examine the wires photomicrographcially to test the soundness of the theory.

Such a photomicrographical study with tungsten is difficult, because here one is not only confronted with preparing the samples for examination of their crystal structure, but this preparation must be good enough to enable one to see any differences in the structure. After many trials a satisfactory result was obtained. The wires were all mounted in a common soft copper frame, and held in position by forcing the copper, between the jaws of a vice, around the wires. In this position they were ground down, polished, and finally etched with boiling hydrogen dioxide. The photographs show a distinct demarcation in the larger samples between the surface layer, and the central portions of the cross sections. In the smaller sections, this surface layer occupies almost all the cross section, and in the smallest wire, the surface structure occupies the whole of the cross section. The radii of the wires varied from 0.00240 to 0.0227 cm.

While it was clearly possible to differentiate between the two crystal states, it was by no means, even with the highest magnifications, to be certain what this change really represented. The surface structure was such that details could scarcely be made out, whereas the outlines of the crystals in the central portions were relatively large, and clearly distinguishable. It is tentatively assumed that the crystals in the surface are extremely small, and separated by an unusually large amount of the so-called amorphous state. This amorphous state is probably groups of atoms, not sufficient in number to constitute genuine crystals. Most metallographers are of the opinion that the amorphous state is the one possessing the higher elasticity.

State University of Iowa,
October 29, 1921.

[1] Phys. Rev., 1, p. 70, 1913; Ia. Acad. Sci. Proc., 24, p. 207, 1917.

A Simplified Method of Correcting for the Decrement of a Decremeter.

By R. R. Ramsey.

In measurement of the decrement of an oscillating circuit the usual formula is

$$d + d_1 = \frac{\pi (C_r - C)}{C_r},$$

where d is the decrement of the circuit to be measured, aërial; d_1 is the decrement of the decremeter; C_r is the capacity in the decremeter circuit which makes the decremeter in resonance with the aërial; and C is the value of the capacity which reduces I^2, the mean value of the square of the current in the decremeter to $\frac{1}{2}I^2$. The method of correcting, usually given in all text books, is the method given by formula 63, page 94, in Radio Instruments and Measurements circular of the Bureau of Standards, No. 74. This formula is complicated and hard to manipulate. Since

$$d = \frac{R}{2L} T,$$

where R is resistance in circuit; L, inductance in circuit; and T, the period of oscillation, then

$$2d = \frac{R_1 + R}{2L} T,$$

when $R_1 = R$. R_1 can be determined by the "half deflection" method of measuring resistance.

Measure the decrement $D_1 = d + d_1$ in the usual method. Introduce resistance in the decremeter circuit until $R_1 = R$, and then measure the decrement again. In this case $D_2 = d + 2d$.

Then $d_1 = D_2 - D_1$.

In determining R_1 the half deflection method is used.[1] If the source is impulse excitation as in the primary of an oscillatory transformer containing a quenched gap, then $I^2R = \frac{1}{2}I^2(R + R_1)$. R_1 is the resistance inserted in the decremeter which reduces I^2 to one half its value.

If the source has small damping as in the secondary of an oscillating transformer or aërial circuit, then $E = IR = \frac{1}{2}I(R + R_1)$ where R_1 is the resistance which reduces the current in the decremeter to one half its value.

Indiana University,
Bloomington.

A New Visual Null Method for Conductivity Determinations.

By Fabian M. Kannenstine and Esme E. Rosaire.

The balance point of an alternating current bridge is indicated by a direct-current galvanometer in an audion circuit. The method is independent of the

[1] Page 182 and page 188, B.S. Circular 74.

frequency impressed on the bridge, thus extending the usable frequencies above the present upper limit of 3,000 cycles per second. When an electrolytic cell was used as one arm of the bridge no difficulty was experienced in balancing with frequencies up to 15,000 cycles per second.

The frequency applied to the bridge is not limited by the characteristics of the human ear. The strain on the observer, incidental to all telephone methods, is eliminated. Readings could be repeated to one part in 50,000 with a galvanometer of only one megohm sensibility.

University of Chicago.

Phase Relations in Coupled Circuits.

By N. H. Williams.

The complete solution of coupled circuits has been given in several different forms by different authors.

The operation of coupled circuits by means of the three electrode vacuum tube for producing sustained oscillations introduces some conditions that are slightly different from those giving rise either to free oscillations or to oscillations forced by an e.m.f. in one of the circuits.

This paper presents a method of measuring the difference in phase between the currents in different parts of a high-frequency system and in particular deals with the difference between the phase relations with positive coupling and those occurring when the coupling is negative.

University of Michigan.

The Change of Mobility of the Positive Ions with Age in Oxygen and Nitrogen.

By Henry A. Erikson.

From results published earlier[1] it is evident that the positive ion, as produced in air at normal pressure by the α particles from polonium, increases in size during the first fraction of a second of its life. The mobilities of the positive and negative ions are nearly the same when measured within an interval of the order of 0.01 second after formation. The normal ratio of 1.37 between the negative and positive mobilities is obtained only after an interval of the order of .01 second. The mobility of the negative ions, when measured at the end of the intervals mentioned above, is found unchanged.

In order to ascertain if the above results are peculiar to air the following investigation of oxygen and nitrogen separately was undertaken. The method used was the same as in the earlier investigations. The ions were carried by means of a current of air between two plates which were at a difference of potential. The ionic current at different down stream distances on one of the plates was measured. By plotting these ionic currents against the corre-

[1] Phys. Rev., XVII., p. 400. Phys. Rev., XVIII., p. 100.

sponding down stream distances a curve is obtained from which it is possible to determine in part the nature of the carriers. The apparatus was enclosed in a vessel which could be filled with the gas under investigation.

The experiments show that both in oxygen and in nitrogen the negative ion does not change. The positive ion, however, does in each case undergo a change. It is also noted that the change in the mobility of the positive ion in oxygen is somewhat more rapid than in nitrogen.

As a working hypothesis the writer assumes that in the process of ionization, an electron is removed from one of the atoms in the molecule. This electron quickly attaches itself to a neutral molecule and this constitutes the negative ion. The positive remainder of the molecule constitutes the initial positive ion. As both of these ions have the same size and charge they move with equal velocities under the action of an electric field. The initial positive ion sooner or later, in a diatomic gas, attaches itself to another atom forming an ion of mass three.

If the velocity of an ion, in any one gas, is inversely proportional to its mass, the ratio of the mobilities of the negative and positive ions should be unity soon after formation. The mobility of the positive ion will then gradually diminish to two thirds the initial value and the ratio of the mobilities becomes 1.33 which is about the final ratio observed in the case of air, nitrogen and oxygen. Postulating N_3 in the case of nitrogen may not however be permissible. In the case of CO_2 the positive ion does not attach itself and the mobility ratio remains unity.

In order to test the above hypothesis the writer is proceeding to investigate as many gases as possible. It is hoped that a sufficient supply of helium may be obtained. This monatomic gas should give evidence as to the validity of the above hypothesis.

UNIVERSITY OF MINNESOTA,
September 5, 1921.

SPHERICAL ABERRATION IN THIN LENSES.

BY T. TOWNSEND SMITH.

IT is well known that the spherical aberration of a thin lens can be expressed in terms of the position of the object, the radii of curvature of the lens, and the index of refraction of the glass, and that the algebraic formula so obtained may be used in the calculation of lens systems in which the aperture is not too large. Somewhat recently Mr. T. Smith[1] of the National Physical Laboratory has called attention to the fact that such calculations have practical value and that in certain cases it is unnecessary to check them by trigonometric computation.

By choosing as the determining factors the focal length of the lens, a shape factor (s), and a position factor (p), (credited to Coddington) it is possible to express the aberration in the form given herewith, where A, B, C, and D are

[1] London Physical Soc., Proc., 30: 119, 1917–18.

constants which involve only the index of refraction:

$$\Delta\left(\frac{1}{v}\right) = \frac{h^2}{f^3}(As^2 + Bsp + Cp^2 + D).$$

The quadratic in this expression is a function which determines the effect of the shape of the lens and of the position of the object upon the longitudinal aberration. By taking proper account of the focal length of the lenses, this function may be used to calculate the spherical aberration of any system of lenses in contact. In particular it may be used to determine the conditions under which the spherical aberration may be eliminated. The calculations may be made analytically or graphically. The graphical work can be simply done and the results are in some cases accurate enough to be used as a guide in the choosing of a suitable combination.

The conditions under which a pair of lenses in contact may be corrected for spherical aberration have been worked out graphically, and curves showing the possible combinations for a distant object have been obtained for a few of the commoner types of optical glass. The condition that the lens pair may be cemented and Taylor's[1] condition for the elimination of coma have been indicated on the diagram. The effect of slight changes in the shapes of the lenses has also been calculated for a lens pair made from the "ordinary crown" and the "dense flint" glasses.

Brace Laboratory, University of Nebraska.

A Low Resistance Connection with a Revolving Shaft.

By A. P. Carman.

The problem was to make an electrical connection with a coil on a revolving shaft, the resistance of the connection to be small and constant. The following device has proved to be practical. In Fig. 1, B is one end of the shaft; a small hole is bored along the axis of the shaft, and the end of the coil is brought to an insulated copper plug P; the rubber or amber bushing RR gives good insulation from the shaft. Extending in the line of the shaft is the wire WW of about 30 cm. length; in most cases No. 25 B. & S. gauge wire was used though No. 20 and No. 30 wires were used with equal success. The wire WW runs through TT a trough of mercury of about 20 cm. length, passing the wire through

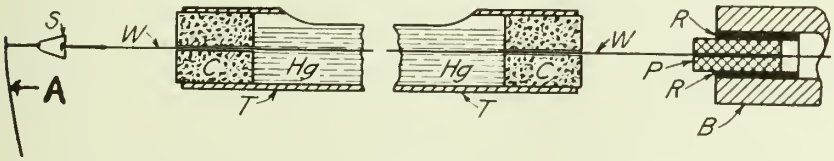

Fig. 1.

ample holes in the corks CC. The wire terminates in a small swivel S, and this swivel is attached to a spring A by which the wire is kept stretched and

[1] H. Dennis Taylor, System of Applied Optics, p. 195, equation (4).

straight. The round pin head turns freely in the hole of the fixed part of the swivel when the shaft rotates. Outside electrical connection is made with the wire by means of the mercury. This device is used on both ends of the shaft so as to complete the circuit. In the first trials, the shaft formed part of the circuit, but there were disturbing thermal and contact electromotive forces at high speed. By completing the circuit with a wire through a hole along the axis of the shaft, these disturbing electromotive forces were eliminated. The following are examples of changes of resistance at rest and at a speed of about 4,000 r.p.m.

R. at rest	.124843	.124391	.123488	.0733497	.072447	.065044
R. at 4000 ± r.p.m.	.132296	.131167	.131167	.972447	.072898	.060948
Differences	.00745	.006776	.007679	.000902	.000451	.000904

These resistances were determined with a Carey-Foster bridge. The different resistances at rest were due to use of different connecting wires *WW*. It is seen that the changes of resistance between rest and motion varied between .5 and .9 of one per cent. of the actual contact resistance at rest, and of course a much smaller percentage of the total resistance of the circuit. Potentiometer measurements showed that the disturbing thermal and contact electromotive forces were very small, of the order not more than one hundred thousandth of a volt. The above contact is being used in an investigation in progress. The device is reported now as it may be important for others in their investigations.

The Effect of Pressure and Gas Content on the Action of Vacuum-tube Detectors.

By H. A. Brown and Chas. T. Knipp.

In recent years there has been put on the market a class of vacuum tubes known as "gas content detector tubes." The advantage of using this type of tube as a detector lies in the fact that it does not require a high-plate voltage for its operation. It is commonly believed that such a tube gives louder response to signals than one having a higher vacuum. It is well known that the low vacuum tubes have critical adjustments of plate voltage and filament current to secure the best response to signal currents. This is not the case for high vacuum tubes. The purpose of the present investigation was to show from experimental data just how the degree of vacuum and the nature of the gas in the tube affect its operation as a detector.

The pressure of the gas in the tube was varied and readings were taken of the plate voltage for the loudest signal response (called the "operating voltage"), and also of the comparative intensity of signal response for various measured pressures. This was done for several tubes of the same type and for tubes of different types and makes. Measurements of the operating voltage

versus pressure were also made with different gases successively introduced into the same tube.

The effect of various pressures and kinds of gas upon the critical adjustment characteristics was also measured. The intensity of response passes through a maximum for each pressure as plate voltage or filament current increases. Different gases were successively introduced into the same tube and measurements were made of comparative best signal response for each gas. The results were arrived at after repeating the test for several tubes, and are summarized at the end of this abstract. Measurements were made of the amplification constant and mutual conductance of different tubes with varying plate voltages for different pressures. If the amplification constant is a function of the geometry of the tube, the presence of gas alters the *effective* geometry of the tube as the curves clearly show. When gas is present the amplification constant decreased with increasing filament current above normal values while the measured value of mutual conductance increased. However, the intensity of signal response passed through a maximum for increasing filament current. The variations of the mutual conductance were very similar to the variations of intensity of signal response with varying plate voltage at different pressures. Data were taken which showed that the characteristic humps in the plate current-grid voltage curves for tubes containing gas were not present when the tube content was helium, the filament being tungsten, nor were humps present for oxide-coated filament tubes containing neon or air.

The tabulated conclusions from the results obtained follow:

1. The degree of vacuum in a detector tube is important. A pressure of ·0025 to .005 mm. of mercury gives two to three times as loud response as does a pressure of .05 mm. of mercury.

2. The operating voltage for the most desirable vacua above mentioned is 40 to 50 volts.

3. The adjustments of operating voltage and best filament current are much easier at the above degrees of vacua, and this fact, with the doubled intensity of audible response, fully justifies the provision of a higher plate voltage than is now needed for many low vacuum detector tubes.

4. The operating voltage varies with the pressure in the tube along a curve of the form $E_0 = e_i(a)^{1/P}$. E_0 is the operating voltage, e_i is probably the ionizing potential of the gas, P is the pressure, and "a" is constant. For various gases the variation gives very similar curves.

5. The bend in the above curve occurs at the point of best audibility of response, or .003 to .005 mm. of mercury, and operating voltages of about 40 to 50 volts. To the right of the bend (increasing pressure) adjustments of operating voltage and filament current become critical.

6. The introduction of neon, nitrogen, or carbon dioxide does not show any change in audibility or intensity of response from that obtained with air in the tube. Argon gives a somewhat louder response, and helium a slightly weaker response.

7. Hydrogen gives a very much weaker audibility of response.

8. The degree of critical adjustment of plate voltage and filament current for best response is about the same for air, nitrogen, neon, and carbon dioxide. Hydrogen tubes are somewhat more critical.

9. The operating voltage is approximately 30 per cent. higher for helium-filled tubes than for those mentioned above at the same degree of vacuum.

10. The operating voltage is considerably less critical for helium-filled tubes than for any other gas content, and compares with those tubes having fair vacuum.

11. Mercury vapor gives better signal response than the other gases tried, while for the former the operating voltage is lower at similar pressures. The operating voltage for mercury vapor varies from 16 to 22 volts depending on the vapor pressure and hence on the temperature of the walls of the tube. The operating voltage and best filament current are also less critical for mercury vapor than for neon, argon, air, or carbon dioxide.

12. For all of the gases tried the audibility of signal response rises to a maximum as the pressure is lowered below .005 mm. of mercury.

13. The operating voltage at low vacuum depends on the ionization potential of the gas in the tube, but the former is about five or six volts higher than the latter up to pressures of .06 to .08 mm. of mercury. Comparative operating voltages for helium, argon, neon, and mercury vapor tube content show this to be true.

Several other interesting results, and a full discussion of the various factors entering and precautions observed, are described in the extended paper which will be published soon.

UNIVERSITY OF ILLINOIS,
August, 1921.

SOME REMARKS ON ELECTROMAGNETIC INDUCTION.

BY S. J. BARNETT.

THIS paper is devoted to historical, critical, and expository comments on matters connected with experiments previously made by the author in various parts of the field of electromagnetic induction.

Experiments *on the motion of insulators in magnetic fields* by Faraday, Blandlot, H. A. Wilson, M. Wilson, and the author are referred to, and the theory is given in sufficient detail to show that the interpretation given by Larmor and Wilson is not tenable. Theoretical difficulties involved in Hertz's theory are pointed out. An additional observation made by the author is described.

Attention is called to the facts that the author's experiments *on electromagnetic induction in the case of rotary motion*, often misquoted, were *not* made to solve the so-called problem of unipolar induction, and that the results obtained were clearly stated in the original paper to be in accord with current

electrical theory, viz., that of Maxwell and Lorentz. The complete clearing up of the problem of unipolar induction on the theoretical side is attributed to Larmor and Pegram. Reference is made to a recent paper on the subject by Swann, which gives the theory in detail, but contains little new material. The author's interpretation of his own experiments is given; and his earlier demonstration that they could not be used to settle the problem of unipolar induction is referred to, with critical comments.

The author's experiments *on electromagnetic induction and translatory motion* are briefly described and his earlier and later interpretations are referred to. The latter is identical with the interpretation published much later by Swann. The theory for both a strictly two-dimensional field and the actual case of the experiments is given according to Maxwell's theory by the method of the vector potential.

The results of the experiments on rotary and translatory motion are contrasted.

Carnegie Institution.

The Existence of Small Ions of Very High Mobilities.

By Oswald Blackwood.

Small ions of very high mobility have been found by Nolan[1] in the ionization from water spray and from radioactive bodies. He finds values more than *seven times* larger than that commonly accepted.

The results for spray ions are interesting since this field has been little explored. The ionization from radioactive bodies, however, has been investigated by many workers using methods much more precise than Nolan's. To the writer's knowledge no one has ever found such large values for ions in undried air. Since they have used methods which are much more accurate than Nolan's, the reality of his ions cannot be admitted even tentatively until their existence has been verified by other methods.

The writer presents evidence indicating that the results are, in fact, capable of another interpretation.

The apparatus consists of a plate condenser 25 cm. long and 10 cm. high, the upper plate being connected to an electrometer, while the potential of the lower one may be given any desired value. The radium emanation is contained in a leaden trough near one end of the charged plate. One centimeter above this trough is a lead shield which is supposed to limit the production of ions to the small volume immediately below it. A steady air current passes through the condenser carrying the ions forward while the electric field drives them vertically. At a critical voltage the beam of ions arrives at the electrometer plate and the current achieves its maximum value.

Nolan finds that the ions are driven to the plate when the voltage is far

[1] Proc. Royal Irish Acad., Vol. XXXIII. (*A*) (1916); Proc. Royal Society (*A*), Vol. XCIV., p. 112 (1918); Proc. Royal Irish Acad., Vol. XXXV. (*A*), p. 38 (1920).

below its critical value. He assumes that this indicates the presence of high velocity ions. The writer, however, shows conclusively that it is due to the fact that ions are produced not only in the constricted space below the shield, but also throughout the entire volume of the condenser. A wire screen electrically connected to the lower plate was placed one centimeter above it so that no ions produced under the lead shield should reach the electrometer plate. This screening reduced the electrometer current to only 75 per cent. of its former value, which showed beyond doubt that most of the ionization is produced in the upper part of the condenser. The difference between the two readings gives the electrometer current due to the ions formed near the lower plate. This corrected curve cuts the axis at the theoretical critical voltage and gives the commonly accepted mobility value for the small ion.

THE UNIVERSITY OF PITTSBURGH.

EFFECT OF LUNAR GRAVITY UPON A QUARTZ THREAD BALANCE.

BY R. C. HARTSOUGH.

The Construction and Description of the Apparatus.—The construction of the balance is somewhat after Threlfall's "gravity balance." The chief addition is a long vertical lever arm and suspended mirror for magnifying small movements. This is due to Lord Kelvin in his "Lunar Disturbance of Gravity" experiments.

The shape of the apparatus is of a large T, the horizontal part is 60 cm. long and the vertical part is 50 cm. long. Instead of silvering, plating and soldering the mounting of the quartz thread, type metal was found entirely satisfactory and much surer and quicker of application.

These specifications of the apparatus will give a correct idea of the balance as used.

Size of quartz thread	0.04 mm. diameter
Length of quartz thread	55.7 cm.
Length of short weight-lever	2.0 cm.
Length of long observing-lever	26.5 cm.
Weight on weight-lever	0.10 gm.

Five complete twists were given each end of the quartz thread in order to hold the weight-lever horizontal and the observing-lever perpendicular.

The apparatus was enclosed in a T-shaped tube of brass and was evacuated to 0.03 mm. mercury pressure, and dried with phosphorous petoxide. The apparatus was placed in the basement on a solid base, however, passing trucks gave a very noticeable vibration. The temperature of this room was constant to within one degree in 24 hours. A galvanometer telescope-scale was used for observing deflections. Distance was 60 cm. The following readings and curve are typical of many taken.

Date.	Time.	Scale.	Room Temp.	Remarks.
Nov. 7.....	7:30 A.M.	23.3	19.0° C.	
	8:45 A.M.	26.7	18.5	
	12:00 Noon	22.0	19.0	
	2:30 P.M.	19.2	19.2	
	5:30 P.M.	17.4	19.4	
	6:00 P.M.	16.6	19.5	Moon at zenith 6:12
	6:14 P.M.	15.9	19.5	
	6:20 P.M.	15.8	19.3	
	8:00 P.M.	16.1	19.8	
	9:15 P.M.	16.5	19.8	
Nov. 8.....	6:30 A.M.	22.7	19.3	
	8:00 A.M.	23.5	19.2	

The evidence of this experiment shows that if the earth's gravitational force is balanced against the torque in a quartz fiber, the moon will disturb that balance gradually over 24-hour periods. A maximum decrease of the earth's gravitation occurring with the moon at its upper culmination and a minimum at the moon's lower culmination.

The author expects in the near future to try to detect any lag effect in the gravitation of the moon and the sun.

The facilities of the Laboratory of Physics of the University of Illinois through the courtesy of Professor A. P. Carman were placed at my disposal for this investigation, while the council and help of Dr. C. T. Knipp were a large factor in its success.

Laboratory of Physics,
University of Illinois,
September, 1921.

On the Electrical Properties of Illium.

By Chas. T. Knipp and J. L. Hall.

Illium was first produced in wire form early during the summer of 1921, making possible the measurement of a number of the electrical properties of this remarkable chemically resistant alloy. The wire for these experiments was generously furnished by Professor S. W. Parr, of the Department of Chemistry, University of Illinois. It was of the particular type known as "Illium-B."

The temperature coefficient of illium was found to be .000479 ohm per degree Centigrade. In this determination a wire of length 147.1 cm. and mean diameter .96 mm. (corresponding to No. 16 B. & S. gauge) was used. The range of temperature was from 0 to 70° C. and the value given above is the mean of 13 observations over 10° intervals.

The resistivity, using the same sample on the basis of the resistances measured over the above range of temperature, was found to be, when extrapolated to zero degrees C., 91.61×10^{-6} ohms.

The largest thermoelectromotive force is produced when illium is coupled with constantin. It produces a smaller thermoelectromotive force when coupled with nickel, and smaller still with german silver; while with platinum, copper and chromel there is but little thermoelectromotive force generated, and with manganin none at all.

The illium-constantin couple over the range 0 to 400° C. was found to be almost identical in its behavior with that of copper-constantin.

UNIVERSITY OF ILLINOIS,
August, 1921.

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THE

PHYSICAL REVIEW.

THE EFFECT OF TENSION ON THE CHANGE OF THERMOELECTROMOTIVE FORCES BY MAGNETIZATION.

By Alpheus W. Smith.

Synopsis.

Combined Effect of Tension and Magnetic Field on Thermoelectromotive Force and Resistance of Some Ferro-magnetic Metals.—Wires 10 cm. long and 0.15 cm. in diameter were each held in heavy brass clamps and stretched while placed axially in a vertical solenoid. While determining the electromotive forces, one end was kept at 100°, the other at 0° C. In the case of *nickel*, the effect of tension on the change in resistance (ΔX) and in thermoelectromotive force (ΔE) produced by a longitudinal magnetic field is a decrease for weak fields but an increase for larger fields. For a given tension, the ratios of ΔX to ΔE and to the magnetic change of length (ΔL) are independent of the field strength and therefore seem to depend on the same factor. *Pure iron* shows a parallelism between the effects of tension on ΔE and ΔL; with increasing tension the curves for ΔE as function of the field shift downward so that for sufficiently large tensions ΔE becomes negative throughout. The curve for ΔE may be considered the sum of two effects, associated with two forms of iron, one of which is proportional to ΔL and is affected by tension more than the other. The behavior of *iron-copper alloys* is qualitatively similar to that of iron. *Iron-nickel alloys* behave like iron until the per cent. of Ni is more than 7 when they tend to behave more and more like Ni. For both series of alloys the change of ΔX due to tension is always a decrease.

Relation between the Hall Constant, Specific Resistance and Fractional Change of Thermoelectromotive Force Produced by a Magnetic Field in a Series of Iron-copper Alloys is pointed out. The three properties vary with copper content in a similar way, all showing a cusp for 1.5 per cent. copper.

Electron Theory of Conductivity and Thermoelectromotive Force.—In a *discussion* of the above results it is shown that neither the gas-free theory as given by Heaps nor Bridgman's gap theory explains them satisfactorily. The decrease in resistance with increase of length would be expected, however, if the number of free electrons varies in an inverse manner with the atomic frequency; and ΔE would vary with magnetic field and tension if the atomic frequency and the number of free electrons are not the same functions of the magnetic field at different temperatures and tensions.

THE influence of tension on the resistance, length, permeability and elastic constants of ferromagnetic substances in longitudinal magnetic fields has been frequently studied. Similar observations do

not seem to have been made on the effect of tension on the changes in the thermoelectromotive forces produced by such a magnetic field. In view of the dependence of the resistance and the thermoelectromotive force on each other and on the elastic and magnetic properties of the substance, it seemed of interest to study the variation of the thermoelectromotive forces produced by a longitudinal magnetic field when the substances were sustaining tensions of different amounts.

Methods of Observation.—The specimens to be studied were in the form of thin wires about 10 cms. in length and .15 cm. in diameter. These wires after being fastened to heavy brass rods were suspended axially in a solenoid which was 40 cms. long. The wires lay near the center of the solenoid where the magnetic field was nearly uniform. At a point just below or above the junction of the brass rods and the wires there was soldered a copper wire which with the specimen formed a thermal couple. One junction was kept in a mixture of ice and water and the other in steam at atmospheric pressure. The tensions were applied to the specimens by placing different weights on a scale pan suspended from the wire.

The thermoelectromotive force arising from the couple was nearly balanced by connecting the copper lead wires in the usual manner to a Wolff potentiometer. The thermoelectromotive forces set up by the longitudinal magnetic field were determined by noting the deflection of a sensitive Leeds and Northrup galvanometer of the d'Arsonval type. From this deflection together with the sensibility of the galvanometer the change in thermoelectromotive force produced by the longitudinal magnetic field was calculated. The total electromotive force of the couple was read directly from the potentiometer.

In order to compare the effect of tension on the change of thermoelectromotive force with the effect of tension on the longitudinal change of resistance, some observations were made on the change of resistance in a magnetic field in these same wires when the wires were sustaining loads of different amounts. The measurements of the changes of resistance were made by means of a Kelvin double bridge. The bridge was balanced as nearly as possible when there was no magnetic field in the solenoid. The deflection of the galvanometer resulting from the establishment of the magnetic field in the solenoid gives a measure of the change of resistance in the specimen resulting from the action of the magnetic field. To calculate the change of resistance from this deflection it is necessary to know the current in the specimen and the sensitivity of the galvanometer besides the resistances entering into the network of the bridge. For resistances of the magnitude used in these

experiments the change of resistance can be calculated with sufficient accuracy from the formula,[1]

$$\frac{\Delta X}{X} = \frac{K}{PI_b}\left[R_g\left(1 + \frac{N}{M}\right) + 2N\right]D,$$

where K = current to produce 1 cm. deflection,
D = deflection of galvanometer in cms.,
R_g = resistance of galvanometer,
I_b = current in the unknown resistance,
N, M and P = resistances in the arms of bridge.

Besides nickel and iron a number of alloys of iron and copper and also some alloys of nickel and iron were studied. These are the same alloys which were used by the author in a study of the Hall effect and the Nernst effect.[2] They were prepared by Burgess and Aston[3] from exceptionally pure metals. The observations on the change of resistance were made at room temperature. The changes in the thermoelectromotive forces are the changes which arise when one junction is at 0° C. and the other at 100° C. The tensions which have been recorded on the following curves have been expressed in kilograms per sq. mm.

The curves in Fig. 1 show the change of resistance and the change of

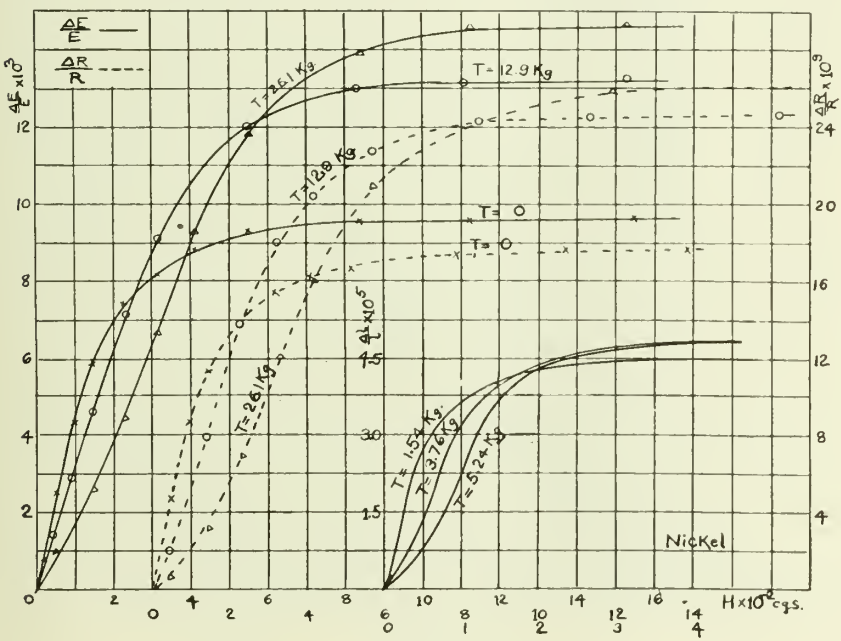

Fig. 1.

[1] Laws, Electrical Measurements, p. 194.
[2] Smith, Phys. Rev. (2), 17, 23, 1921.
[3] Burgess and Aston, Met. and Chem. Eng., 8, 19, 1910.

thermoelectromotive force in nickel under different loads in a longitudinal magnetic field. This nickel was of unknown purity. It was obtained from Eimer and Amend as pure nickel. For the sake of comparison there has been plotted in this same figure the fractional change of length in nickel in a longitudinal magnetic field. The data for these curves were taken from the work of Honda and Terada.[1] These curves have been plotted above the horizontal axis without regard to the sign of the effect whether positive or negative. The magnetic field produces an increase in the resistance, a decrease in the thermoelectric height against copper and a decrease in length. An examination of these curves shows that the change in thermoelectromotive forces produced by a longitudinal magnetic field behave in almost exactly the same way in which the change of resistance and the change of length behave. The effect of tension is to decrease the effect of the magnetic field on the resistance, length and thermoelectromotive forces for smaller magnetic fields. On

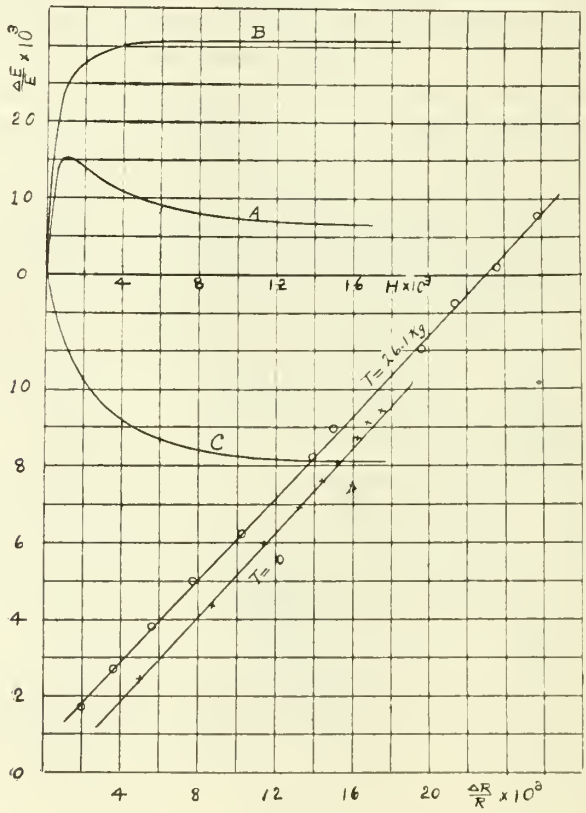

Fig. 2.

[1] Honda and Terada, Phil. Mag. (6), 13, 36, 1907.

the other hand for the larger magnetic fields these changes are greater for large tensions than for small tensions.

In the lower half of Fig. 2 the fractional change of resistance for a particular magnetic field has been plotted against the fractional change of thermoelectromotive force, for the case in which the wire is unloaded and for the case in which the wire sustains the maximum load. A proportionality is found between these two changes. The factor of proportionality is a function of the tension. Heaps[1] has pointed out that there is in nickel a proportionality, except for small magnetic fields, between the change of resistance and the change of length. To these observations is added the fact that in nickel the change in thermoelectromotive force is proportional to both the change of resistance and the change of length. From this it is clear that whatever factors determine the change of length of nickel, in much the same way they determine the change of resistance and the change of thermoelectromotive force. Grondall,[2] however, failed to find a simple relation between the change in length and the change in thermoelectromotive forces in Heusler alloys.

Similar observations on pure iron show a parallelism between the change of thermoelectromotive force produced by the magnetic field when the wire sustains different loads and the change in length under corresponding conditions. The curves at the bottom of Fig. 3 are taken

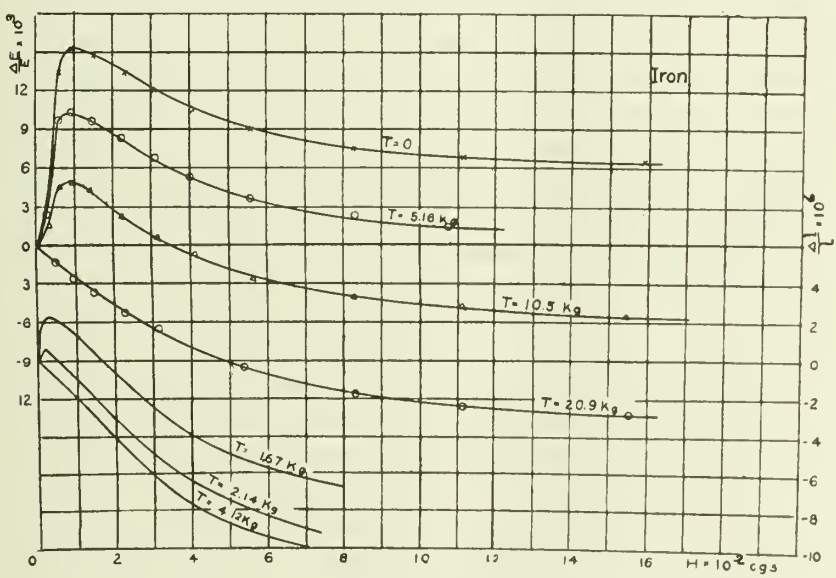

Fig. 3.

[1] Heaps, Phys. Rev. (2), 6, 34, 1915.

[2] Grondall, Phys. Rev. (2), 4, 325, 1914.

from the work of Honda and Terada. A comparison of these curves with those above them shows that the effect of tension on the change of length in a magnetic field and its effect on the change in the thermoelectromotive force are quite similar. In each case the application of tension decreases the initial effect. When the tension is sufficiently large the direction of the change is reversed. The initial change of the length is an elongation and this at sufficiently large fields and tensions becomes a contraction. The initial change in the thermoelectromotive force is an increase in the thermoelectric power with respect to copper. For sufficiently large magnetic fields and tensions this reverses and becomes a decrease. An increase in length is associated with increase in thermoelectric power. The larger the tension the smaller the magnetic field at which this reversal takes place. The reversal of the direction of the change of length takes place for smaller tensions and smaller magnetic fields than those necessary for the reversal of the direction of the change of thermoelectromotive force. This may be due to the fact that the two changes were not studied in the same specimen of iron. For sufficiently large tensions the curve starts downward from the origin and the change of length is always a contraction and the thermoelectric power is always decreased.

The linear relation between the change of length, resistance and thermoelectromotive force found in the case of nickel does not hold in the case of iron. The curves (Fig. 9) showing the relation between the change of resistance and the magnetic field have the usual form for iron. The application of tension causes a decrease in the change of resistance produced by the magnetic action. In nickel tension caused a decrease in the change of resistance which was later followed by an increase at sufficiently large magnetic fields. Heaps[1] found a proportionality between the change of length and the change of resistance in a longitudinal magnetic field. The curve which he gives to show the relation between the change of length and the magnetic field is very different from those given by other observers except for one case recorded by Bidwell.[2] The reason for the discrepancies between the observations of Heaps and those of other observers is not evident, unless it be due to polymorphism of iron and in one of these forms the change is positive and in the other it is negative.

Now each of these curves showing the relation between the change of length and the change of thermoelectric power in iron in a longitudinal magnetic field can be arbitrarily broken up into two parts as shown in the upper half of Fig. 2. This is equivalent to regarding the magneto-

[1] Heaps, PHYS. REV. (2), 6, 34, 1915.

[2] Bidwell, Proc. Roy. Soc., 56, 1894.

strictive effect as well as the change in thermoelectric power as made up of two parts, one positive and the other negative. One of these parts is represented by Curve *B* and the other by Curve *C*.

The sum of the ordinates of Curve *B* and Curve *C* gives the ordinates of the observed Curve *A*. If this analysis is correct it may be that for some reason the part of the total effect represented by Curve *B* was negligible in the specimen studied by Heaps. In view of the polymorphic character of iron this is not improbable. This would leave the curve *C* which corresponds to his observations. If such a splitting up of the effects into two parts is allowable it may be that there is still a proportionality between the change of resistance and one of the terms entering into the observed change of length and thermoelectromotive force. This analysis is the more probable in view of the effect of tension on the change of length and on the change of resistance. This effect of tension might be interpreted as decreasing that part of the effect represented by Curve *B* and leaving the second part essentially unchanged. When the tension was made large enough, a reversal of the change would then follow for sufficiently large magnetic fields. It would also follow that the larger the tension the smaller the magnetic field necessary to reverse the effect. If the tension were made large enough to render the first part of the effect represented by Curve *B* negligible in comparison with the second part represented by Curve *C*, the change of length and the change of thermoelectromotive force would always have the same sign and might be represented by the observed curves as found for large values of the tension.

In Figs. 4, 5, 6, 7 and 8 are given curves showing the change in the thermoelectromotive force as a function of the magnetic field for six alloys of iron and copper and three alloys of iron and nickel. All of these curves except those for the alloy containing 93 per cent. iron and 7 per cent. nickel and the alloy containing 88.7 per cent. iron and 11.3 per cent. nickel have the characteristics of the corresponding curves for pure iron. The addition of copper to iron changes the magnitude of the effect of a given longitudinal magnetic field on the thermoelectric power but in other respects the behavior of the alloys is very similar to the behavior of the iron. The direction of the thermoelectromotive force and also the direction of its change in the magnetic field is the same in these alloys as in pure iron. The addition of copper to iron at first increases the effect of the longitudinal magnetic field on the thermoelectromotive force. After the alloy contains 1.5 per cent. copper a further increase in the concentration of copper decreases the change in thermoelectromotive force.

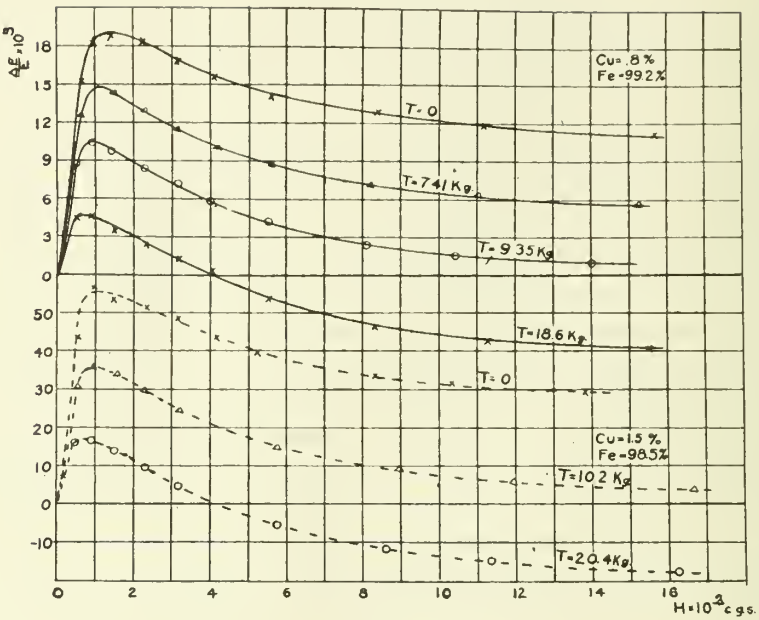
ΔE/E ×10³
Cu=.8%
Fe=99.2%
T=0
T=7.41 Kg
T=9.35 Kg
T=18.6 Kg
T=0
Cu=1.5%
Fe=98.5%
T=10.2 Kg
T=20.4 Kg
H×10⁻² c.g.s.

Fig. 4.

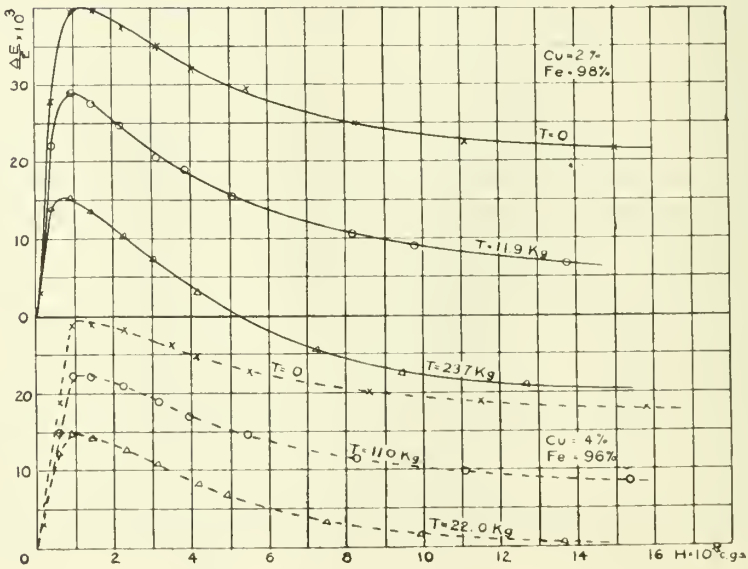
ΔE/E ×10³
Cu=2%
Fe=98%
T=0
T=11.9 Kg
T=23.7 Kg
T=0
T=11.0 Kg
Cu=4%
Fe=96%
T=22.0 Kg
H×10⁻² c.g.s.

Fig. 5.

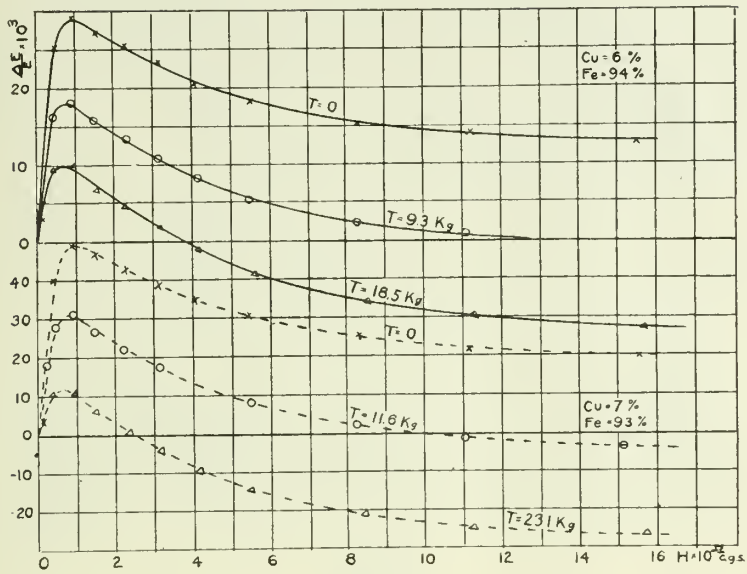
ΔE × 10³
Cu = 6 %
Fe = 94 %
T = 0
T = 9.3 Kg
T = 18.5 Kg
T = 0
T = 11.6 Kg
T = 23.1 Kg
Cu = 7 %
Fe = 93 %
H × 10³ c.g.s.

Fig. 6.

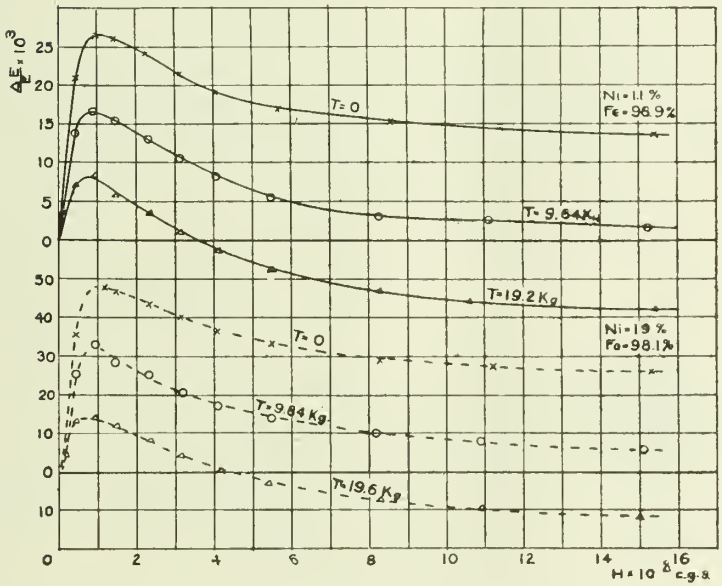
ΔE × 10³
Ni = 1.1 %
Fe = 98.9 %
T = 0
T = 9.64 Kg
T = 19.2 Kg
Ni = 1.9 %
Fe = 98.1 %
T = 0
T = 9.84 Kg
T = 19.6 Kg
H × 10³ c.g.s.

Fig. 7.

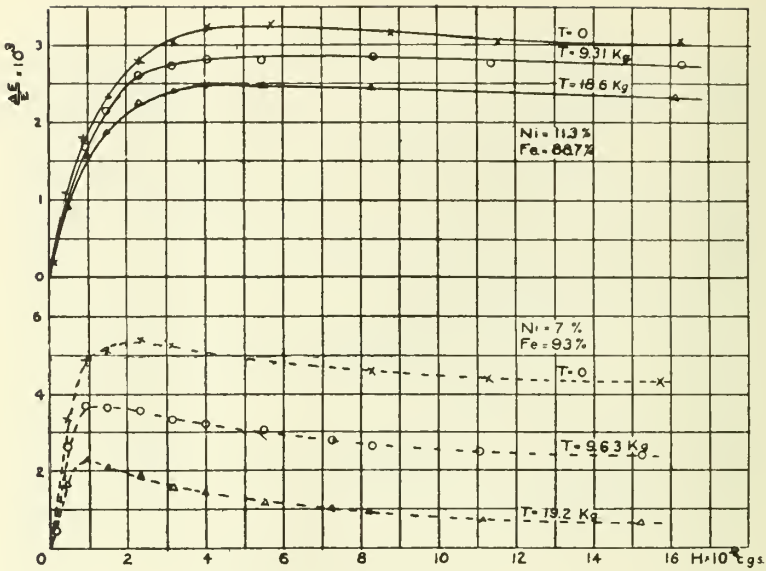

Fig. 8.

The addition of nickel to iron in small quantities causes an increase in the magnitude of the effect over that observed in pure iron. The direction of the thermoelectromotive force and the direction of its change in a magnetic field remain the same as in pure iron until the alloy contains about 7 per cent. nickel where a reversal of direction takes place in both. The alloy then begins to behave more like pure nickel. It still retains some of the characteristics of iron, passing through a maximum and showing a tendency to reverse its direction for sufficiently large tensions. An alloy containing 11.3 per cent. nickel and 88.7 per cent. iron shows more clearly the characteristics of nickel. The effect passes through a maximum as in the other sets of curves but the decrease after the maximum is passed is very gradual. The application of tension causes a decrease in the magnitude of the effect for all values of the magnetic field while in nickel it caused a decrease for low fields and an increase for large fields. The reversal of direction obtained in the preceding cases can not be realized in these alloys.

The longitudinal change of resistance in two of these copper-iron alloys has been represented in Fig. 9 and the observations on the nickel-iron alloys in Fig. 10. In each case the application of tension decreases the change of resistance. The change of resistance when the specimen is completely magnetized is somewhat smaller in those alloys which contain the greater percentage of copper. On the other hand the initial value of this change of resistance in pure iron for low magnetic fields is somewhat

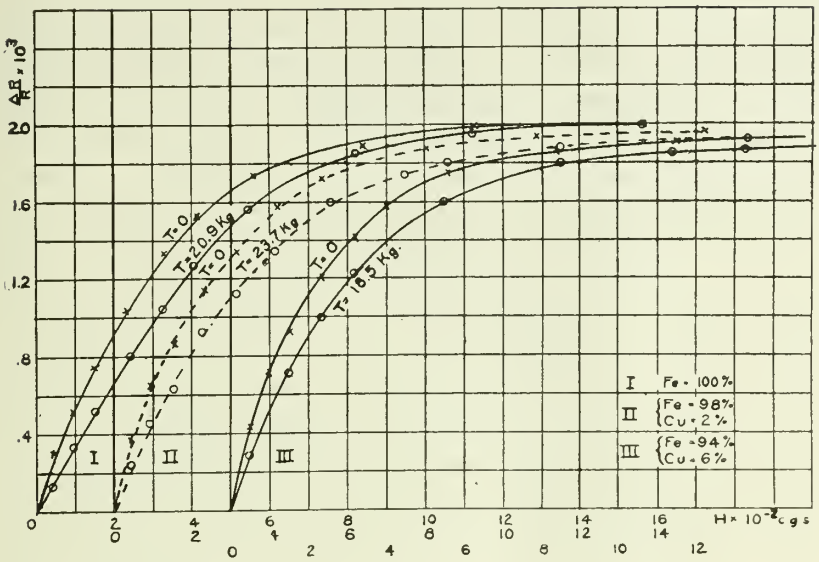
ΔR/R × 10³
2.0
1.6
1.2
.8
.4
T=0
T=20.9 Kg
T=0
T=23.7 Kg
T=0
T=18.5 Kg
I
II
III
I Fe = 100%
II Fe = 98% Cu = 2%
III Fe = 94% Cu = 6%
H × 10⁻² c g s

Fig. 9.

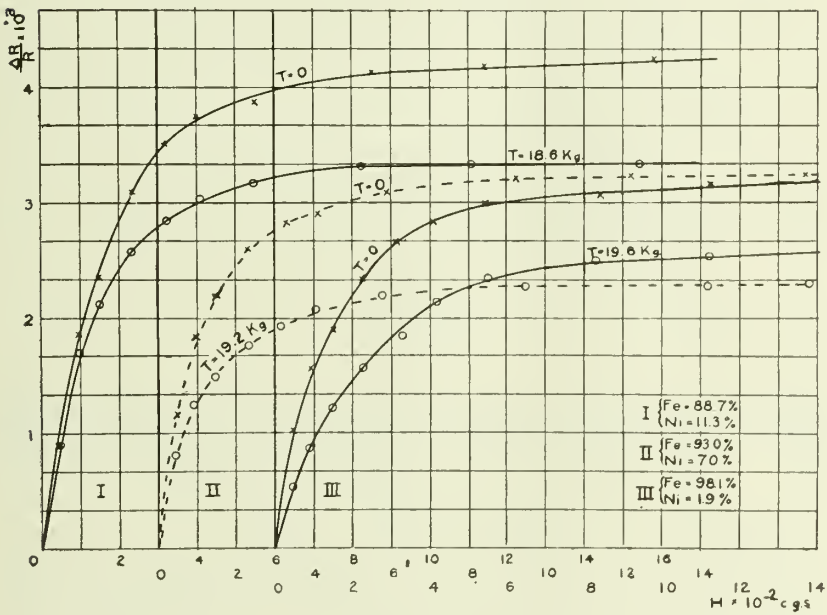
ΔR/R × 10³
4
3
2
1
T=0
T=18.6 Kg
T=0
T=19.2 Kg
T=0
T=19.6 Kg
I
II
III
I Fe = 88.7% Ni = 11.3%
II Fe = 93.0% Ni = 7.0%
III Fe = 98.1% Ni = 1.9%
H × 10⁻² c g s

Fig. 10.

less than it is in the alloys containing copper. From Fig. 10 it is seen that the addition of nickel to iron increases the change of resistance produced by the magnetic field. It is also seen that the effect of tension is greatest where the amount of nickel is largest.

The upper curve of Fig. 11 shows the Hall constant as a function of the

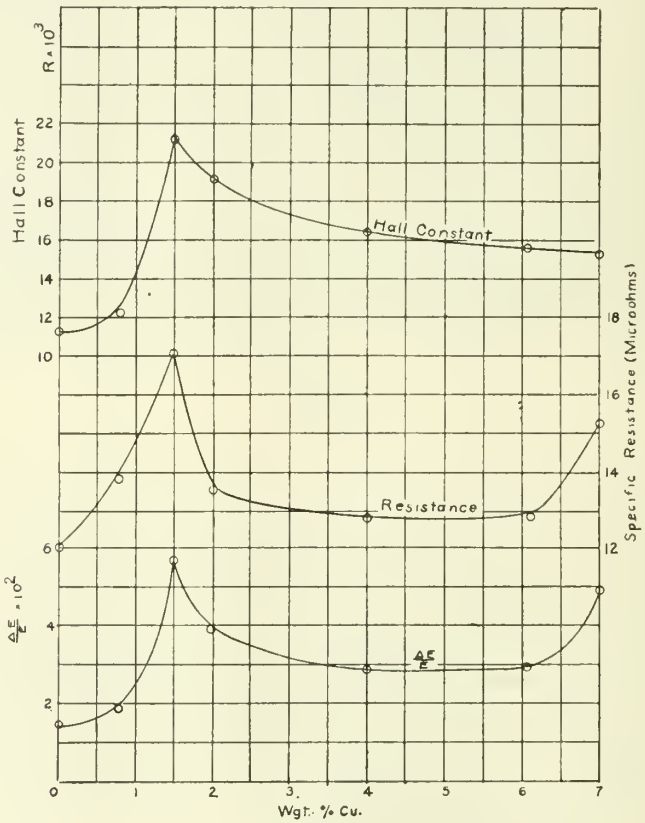

Fig. 11.

concentration of copper. This curve is taken from a former paper by the author.[1] The middle curve represents the specific resistance of these alloys. These resistances were determined by Burgess and Aston.[2] In the lower curve the fractional change in the thermoelectromotive force has been plotted against the concentration of the copper in the alloys. These changes in thermoelectromotive forces are those produced by a magnetic field of 98 gauss when the wire was not under tension. The similarity between these curves is quite evident. They have essentially

[1] Smith, PHYS. REV. (2), 17, 23, 1921.

[2] Burgess and Aston, Met. and Chem. Eng., 8, 79, 1910.

the same characteristics. There is a cusp in each curve where the alloy contains 1.5 per cent. copper. This interrelation for which there seems to be no satisfactory explanation indicates a dependence of all of these effects on some common property of the metals and alloys.

Discussion of Results.—The sources which may be thought of as operating to produce these changes of length, resistance and thermoelectromotive force are changes in the mean free path of the electron, in the number of electrons, in the amplitude of vibration of the atoms and in their frequency of vibration. The change in the mean free path of the electrons would arise from the molecular rearrangement and also from the change in path produced by the action of the magnetic field on the electrons. From this point of view the molecular rearrangement with its accompanying changes in the electric and magnetic forces would be entirely responsible for the change of length and a parallelism between the change of length and the change of resistance would be expected only when the influence of the molecular rearrangement on the mean free path is large in comparison with the effect of the magnetic field on the mean free path.

The application of tension might be expected to decrease the effect of the magnetic field on molecular rearrangement and so decrease the change of resistance and change of length arising out of molecular rearrangement. Since it has been seen that the observed effect in iron and in the iron-copper alloys may be regarded as made up of two parts and that one of these parts seems to be nearly wiped out by sufficiently large tensions it may be that part of the total effect represented by Curve *A* (Fig. 2) arises out of molecular rearrangement produced by the magnetic field. In view of the fact that this part of the effect is missing in nickel it would then be necessary to conclude from this point of view that molecular rearrangement gives rise to a small part of the effect in nickel.

Assuming that the number of free electrons is not changed by the action of the magnetic field Heaps[1] finds on the basis of the gas-free electron theory a proportionality between the fractional change of resistance and the fractional change of length in a longitudinal magnetic field. He thus arrives at the relation,

$$\frac{\Delta R}{R} = -\frac{\Delta\lambda}{\lambda} = -C\frac{\Delta l}{l},$$

where ΔR is change of resistance,

λ and $\Delta\lambda$ are mean free path and change of mean free path respectively,

l and Δl are length and change of length respectively.

[1] Heaps, Phys. Rev. (2), 6, 34, 1915.

Here it is seen that an increase in resistance is associated with a decrease in mean free path and a corresponding decrease in length.

If one holds to the constancy of the number of free electrons in the magnetic field it is not possible to explain the parallelism between the change of length, change of resistance and change of thermoelectromotive force on the basis of the gas-free electron theory. If, however, the number of free electrons is a function of the magnetic field and not the same function at different temperatures then the application of the magnetic field might set up a thermoelectromotive force between the ends of the wire. On the basis of these experiments showing the change in the thermoelectromotive force in a magnetic field it seems impossible to accept the assumption of Heaps that the number of free electrons is independent of the magnetic field.

It is of interest to consider these observations in connection with the gap theory of electric conduction developed by Bridgman.[1] From the point of view of this theory it is considered that the electrons pass without resistance through the atom and that the vibrations of the atoms determine the chance that an electron may pass from one atom to the next. This chance is a function of the amplitude of atomic vibration and of the distance from atom to atom. The greater the mean distance between atomic centers the greater the difficulty which the electron encounters in jumping the gap. It is, however, assumed that when the atoms are at rest the electrons encounter no resistance in passing across the gap provided the separation of atomic centers is not too great. If the mean distance between the atomic centers alone determines the probability that an electron pass from atom to atom, an elongation produced by the magnetic field would be associated with an increase in resistance, since the greater the distance between the atoms the greater the resistance of the metal. But in the case of nickel and possibly in the case of iron it has been seen that a contraction has been accompanied by an increase in resistance. It would, therefore, be necessary to conclude that the amplitude of vibration of the atoms is the controlling factor in determining these changes. The vibrations of the atoms might easily be considered different in the magnetic field from their vibrations in the absence of the field. Now the magnetic field produces an increase of resistance and Bridgman finds that the resistance is proportional to the square of the amplitude of vibration. Since the resistance is increased by the magnetic field it would follow from this theory that the amplitude of vibration has been increased by the magnetic field. Since with this increase in resistance there has been found to be associated a decrease in length and therefore a decrease in the distance between atomic centers we are

[1] Bridgman, PHYS. REV., N.S., 17, 161, 1921.

forced to conclude that the amplitude of vibration is greatest where the distance between the atoms is least. This does not seem to be a very reasonable conclusion unless the considerations introduced by Bridgman to explain the anomalous behavior of bismuth and antimony under pressure be carried over to the explanation of this difficulty. Accepting the assumptions of Grüneisen, Bridgman concludes that in these cases it may be possible to have an increasing amplitude of vibration with an increasing pressure and therefore an increase in resistance. The same reasoning would account for the fact that a contraction in the magnetic field is associated with an increase of resistance. This method of reasoning on the whole does not seem very satisfactory and it is necessary to conclude that the gap theory of electric conduction does not give a very satisfactory explanation of the fact that a decrease in length accompanies an increase in resistance in the magnetic field. In its present development this theory does not cover thermoelectric effects and has therefore no suggestion with respect to the relation between the change in thermoelectromotive forces and changes of resistance and length.

Another line of attack lies in assuming that the number of free electrons is a function of the frequency of the atom and that this frequency is changed by the application of tension and also by the magnetic field. The magnetic field produces a change in the orientation of the molecules and probably a change in the electric and magnetic forces acting in the interstices between the atoms. An elongation accompanying magnetization would increase the distance between the atoms and consequently decrease the electric and magnetic forces operating in the vacant spaces between the atoms. This decrease in the electric and magnetic forces would also produce a decrease in the frequency of vibration of the atom. If it be assumed, in agreement with March,[1] that an increase in the frequency causes a decrease in the number of free electrons, a contraction caused by the longitudinal magnetic field will be accompanied by an increase of resistance. This result is in agreement with the observations on nickel. This point of view would also offer a possible explanation of the change in thermoelectromotive force. When there is a change in the number of free electrons due to an elongation or a contraction of the metal in a magnetic field there would be a change in the concentration of the electrons. Since the wire is unequally heated this change in concentration might not be the same at the hot and the cold junctions. Hence thermoelectromotive forces would be set up. Their direction would depend on whether the magnetic field produced greater or less changes in the concentration as the temperature is increased.

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[1] March, Ann. d. Phys. 49, 710, 1916.

THE LUMINESCENCE OF INCANDESCENT SOLIDS.

By E. L. Nichols and H. L. Howes.

Synopsis.

Luminescence of Incandescent Oxides.—Some oxides, when heated to a temperature lying within a definite and sometimes narrow range, emit radiation in a limited region of the spectrum far in excess of the radiation emitted in that region by a black body at the same temperature. The excess is ascribed to luminescence. As a striking example, the blue radiation from niobium oxide at 560° C. is about 85,000 times the corresponding radiation from a black body, the ratio decreasing with increasing temperature until it is 1.35 at 1037° C. just before the oxide melts.

The oxides of beryllium, magnesium, calcium, aluminum, silicon and zirconium also show a blue glow, relatively strongest at the lowest stage of incandescence, decreasing to a minimum, then increasing to one or two crests corresponding to outbursts of blue luminescence between 1100° and 1500° C.

Intensity-temperature curves for the red, green and blue radiations from the oxides of samarium, gadolinium, gallium, niobium, erbium, cerium, praesodymium and neodymium, from 700° to 1550°, show that all except cerium emit a blue or green-blue glow, and all but niobium and neodymium have one or two red, green and blue outbursts above 1000° C. Luminescence is different from temperature radiation not only in its variation with temperature and in its spectrum distribution but also in showing marked fatigue effects and in varying with the previous heat treatment and with the mode of heating used. The effect for any oxide is also sensitive to slight impurities as shown by tests of a *synthetic ruby* and a crystal of *calcium fluoride* containing rare earths.

Luminescence is probably a phenomenon of instability associated with a chemical change such as oxidation or with the physical disturbances which the oxides undergo as they are heated and which are manifested in changes of electrical conductivity, crystal structure and other properties.

Luminescent Emission Bands of Neodymium Oxide occur approximately at *wavelengths* 525, 550, 570, 615 and 660 $\mu\mu$. At 735° C. these bands were brighter than corresponding black-body radiation, but their excess *intensity* decreased, relatively, with increasing temperature until at 1010° they had disappeared into the continuous background of thermal radiation.

THE following substances when heated to incandescence emit light other than that which they would be capable of radiating as a result of their temperature alone; in a word they are luminescent:

1. The oxides of certain elements (grouped below as they occur in the periodic table):

II.	III.	IV.
Beryllium	——	——
Magnesium	Aluminum	Silicon
Calcium	——	Titanium[1]
Zinc	Gallium	Zirconium

[1] The detailed discussion of the luminescence of titanium oxide is reserved for a later paper.

These are all refractory oxides, white or nearly white in color, *i.e.*, transparent when in mass, as are nearly all known luminescent solids.

Not all refractory, white oxides are luminescent by incandescence however, germanium oxide and thorium oxide, of those tested, having failed to show the effect.

On the other hand it is as yet by no means certain that some oxides of lower melting point such as barium oxide, strontium oxide, etc., do not luminesce at the stages of incandescence of which they are capable. They are not amenable to the methods employed in this paper and the exploration by other means has not been undertaken excepting in the case of zinc oxide.

2. Certain of the rare earths, *i.e.*, gadolinium oxide; samarium oxide; niobium oxide, with tantalum as an admixture; the oxides of praesodymium and of neodymium; the oxides of cerium and of erbium.
3. Certain mixtures such as:—$Al_2O_3 + 2\% \ Cr_2O_3$ (as in synthetic ruby). Calcium Fluoride (a fluorite crystal said to contain the rare earths).

Method of Observation.

The instrument used in detecting luminescence and in determining its brightness was an optical pyrometer, based upon the Morse gauge, in which a tungsten filament in the focal plane of a telescope of short focus, low power but rather large aperture is superimposed upon the image of the surface the brightness of which is to be determined.

With this pyrometer we measured the brightness I_0 of the incandescent oxide under observation and compared the same with the brightness I_{bb} of a black body at the same temperature. Both I_0 and I_{bb} were expressed in terms of the brightness of the black body at 1000° C. which was taken as a convenient arbitrary unit. The emission of the luminescent oxide, as contrasted with that of the black body under like conditions was given by the ratio, I_0/I_{bb}.

For the most direct and positive determination of this ratio observations were made upon the two incandescent surfaces mounted side by side and subjected to precisely the same process of heating. The most satisfactory arrangement was found to be that indicated in Fig. 1 *B*, where the black ring represents a surface of uranium oxide and the inner disk a coating of the oxide to be studied. The image of the filament of the pyrometer lamp is seen against this pattern.

At the red heat, say 700° C., since these white oxides are exceedingly poor radiators, temperature radiation alone would give us the condition

shown in Fig. 1 *A*, where the disk of white oxide is dark compared with the surrounding ring of black oxide and where the filament may be brought to a degree of incandescence such as to be dark against the black body as a background and bright against the central disk. Luminescence of sufficient intensity will reverse this effect as in Fig. 1 *B*.

Fig. 1.
The pyrometer field.

When, as is frequently the case, the luminescence is confined to one end of the spectrum, both appearances may be observed in the same specimen by shifting the color screen in the eyepiece from red to blue. This is true at the lower stages of incandescence for the oxides of beryllium, magnesium, calcium, aluminum, silicon and zirconium.

For these substances it was therefore possible to determine:

1. The actual black-body temperature and the corresponding brightness I_{bb} by settings on the uranium oxide made through a red screen of equivalent wave length .65 μ.
2. The black-body temperature pertaining to the temperature-radiation from the white oxide: this by settings on the white oxide through the red screen.
3. The brightness of luminescence plus temperature radiation by observing through a screen transparent to the wave-lengths of the luminescent glow.

As will be seen later the luminescence was so great as compared with the temperature-radiation up to nearly 1000° C. that the latter could be ignored.

Mode of Heating.

The surfaces under observation were heated by a hydrogen flame impinging upon them vertically and normally from above, the axis of the flame being concentric with the disk of oxide. The flame, which was from a blast lamp of the usual form, was supplied with sufficient oxygen to give it stability and direction. It might be described as an oxy-hydrogen flame with minimum oxygen.

The choice of this means of producing incandescence was not based primarily upon the rapidity with which temperatures up to 1600° C. can be attained, the ease with which they can be maintained nor the facility with which one can pass from one temperature to another.

The main consideration was that the effect we were seeking is only indirectly related to temperature but is greatly stimulated and enhanced by the conditions existing in the oxy-hydrogen flame.

Luminescence versus Temperature-radiation.

For the purposes of this paper all radiation in excess of the black-body radiation pertaining to the temperature in question is to be classed as *luminescence*. Radiation due to temperature alone, *i.e.*, following the recognized laws relating radiation to temperature, will be designated simply as *temperature-radiation*. In other words it will be assumed, in accordance with accustomed usage, that a selective radiator emitting light by virtue of its temperature alone may have regions of its spectrum approaching the intensity of the corresponding regions in the spectrum of a black body at the same temperature but that its brightest bands cannot anywhere pass beyond the envelope which surrounds the energy area for the radiation of the black body in question.

It will suffice then to show that the radiation from the various substances already named surpasses that from a black body, in certain parts of the spectrum and throughout certain definite ranges of temperature, in order to establish the fact that we have to do with some form of luminescence.[1] To that end the simple method of observation already briefly outlined is obviously well adapted.

Luminescence of this sort, which is superimposed upon the temperature-radiation of the substance, appears and after increasing to a maximum disappears within a definite and often a comparatively narrow

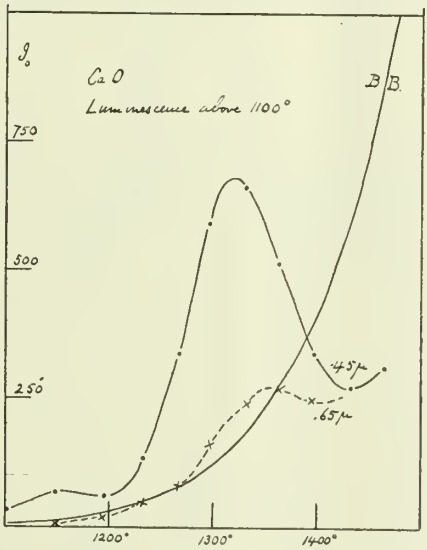


Fig. 2.

Luminescence superimposed on black-body radiation.

[1] Various other characteristics suggestive of the better known types of luminescence will appear in the course of this presentation.

range of temperature. Fig. 2 illustrates such an outburst of luminescence from calcium oxide at about 1300° C.

In this diagram the curve B.B. represents the normal increase in brightness of a black body between 1100° and 1500°. The other curves indicate the brightness of the glowing oxide in the red (.65 μ) and in the blue (.45 μ). It may be noted that *in passing from 1300° to 1400° the calcium oxide, instead of increasing in brightness according to the law of temperature radiation, actually falls off* about fifty per cent.

It had been our purpose in these measurements to separate luminescence as fully as possible from temperature radiation by selecting mutually exclusive screens and this separation is very thoroughly accomplished in the case of the six oxides just mentioned, at least for temperatures below 1000°. In this outburst depicted in Fig. 2 it will be seen that even the red end of the spectrum is somewhat enhanced.

The Blue Glow.

At the lowest temperatures at which visible radiation from these oxides can be detected the ratio I_0/I_{bb} reaches extraordinary values. The blue of the spectrum (luminescence) is many times, often many hundreds

Table I.

Luminescence of Beryllium Oxide and Magnesium Oxide.

Temp. C.	BeO.				MgO.			
	I_0.		I_0/I_{bb}.		I_0.		I_0/I_{bb}.	
	Red.	Blue.	Red.	Blue.	Red.	Blue.	Red.	Blue.
665°	.00000025	.0563	.000195	473	.00000018	.0202	.00140	156.7
735°	.0000016	.0795	.000867	65.8	.000026	.0320	.00214	45.0
837°	.00067	.295	.0271	12.0	.00033	.423	.0135	17.2
960°	.038	1.44	.0832	3.14	.0202	3.63	.0482	8.77
1037°	.210	1.95	.109	1.00	.165	8.91	.0847	4.57
1097°	1.00	3.31	.169	.561	1.077	16.1	.182	2.72
1145°	2.46	6.73	.186	.511	....	....	....	....
1190°	6.75	13.0	.252	.423	9.77	26.4	.367	1.04
1228°	72.5	110	1.580	2.44	....	....	....	....
1263°	146	180	1.91	2.35	26.6	36.7	.347	.479
1294°	229	230	1.87	1.99	....	....	....	....
1328°	295	254	1.66	1.43	55.6	72.0	.312	.404
1394°	513	.316	1.32	.813	122.9	139	.257	.356
1429°	....	....	....	....	182	194	.313	.333
1462°	767	513	.927	.620	285	277	.344	.334
1488°	910	600	.830	.535	...	...	....	....
1527°	1,181	773	.728	.477	745	525	.460	.324
1580°	1,641	1,052	.610	.391	1,614	1,012	.600	.375
1606°	1,928	1,282	.564	.375	2,309	1,387	.675	.406

of times, brighter than the corresponding regions of the spectrum of the black body at the temperature in question while the temperature-radiation from the oxide, as indicated by the intensity of the red end of the spectrum, is only a few thousandths of that from the black body. That this is a general statement for these oxides may be seen from the following tables (see values for 665° and 735°).

In Tables I., II. and III. are given the brightness I_0 of six of the oxides under consideration at wave lengths .45 μ and .65 μ, at various temperatures up to about 1600°; also the ratio I_0/I_{bb} throughout this range.

TABLE II.

Luminescence of Calcium Oxide and Aluminum Oxide.

Temp. C.	CaO.				Al_2O_3.			
	I_o.		I_o/I_{bb}.		I_o.		I_o/I_{bb}.	
	Red.	Blue.	Red.	Blue.	Red.	Blue.	Red.	Blue.
665°	.0000006	.0278	.00432	216	....	....	....	400
735°	.000016	.0646	.01285	52.2	.000026	.083	.0213	67.3
837°	.00292	.336	.114	13.7	.000795	.191	.0324	7.80
960°	.1000	1.46	.240	3.49	.173	1.54	.377	3.36
1037°	.802	7.31	.411	3.75	1.25	6.95	.639	3.56
1097°	2.69	25.0	.454	4.19	2.63	21.4	.444	3.61
1145°	6.92	41.7	.522	3.11	2.70	22.4	.209	1.73
1190°	17.5	58.2	.656	2.18	4.31	24.4	.162	.916
1228°	33.1	87.6	.725	1.91	9.55	26.9	.209	.590
1263°	40.7	151	.531	1.97	19.7	59.0	.257	.767
1294°	61.7	254	.535	2.20	33.4	76.7	.290	.665
1328°	120	351	.671	1.97	76.5	164	.431	.923
1362°	264	310	.994	1.17	141	141	.531	.531
1394°	345	226	.887	0.582	1,432	530	3.63	1.36
1429°	422	190	.725	.326	....	....	....	....
1462°	507	226	.613	.274	2,240	1,102	2.70	1.33
1488°	624	261	.570	.233	....	....	....	....
1527°	871	327	.536	.202	1,799	1,799	1.11	1.11
1580°	1,225	578	.455	.215	....	....	....	....
1606°	1,429	795	.381	.232	....	....	....	....

These are the substances whose luminescence at the lowest stages of incandescence has been termed the *blue glow*.[1] They are among the poorest temperature-radiators known and when heated are visible chiefly because of their luminescence.

The region designated as "blue" in the columns of Tables I., II. and III. is really a band, the precise limits of which are somewhat difficult to

[1] Nichols and Howes, Journal, Optical Society of America, VI., No. 1, 1922.

TABLE III.

Luminescence of Silicon Dioxide and Zirconium Dioxide.

Temp. C.	SiO_2.				ZrO_2.			
	I_0.		I_0/I_{bb}.		I_0.		I_0/I_{bb}.	
	Red.	Blue.	Red.	Blue.	Red.	Blue.	Red.	Blue.
655°	.00000076	.0382	.00059	195	.0000026	.00684	.0204	53.1
735°	.0000026	.0708	.0021	57.3	.000077	.0382	.0621	30.9
837°	.00059	.341	.0239	13.9	.0039	.403	.161	16.4
960°	.0275	1.65	.0600	3.59	.1210	3.41	.288	8.15
1037°	.191	4.42	.0977	2.26	1.20	6.91	.617	3.50
1097°	1.10	11.0	.186	1.86	6.34	19.2	1.07	3.25
1190°	8.51	35.3	.316	1.33	24.5	87.5	.923	3.29
1263°	41.2	89.1	.537	1.16	59.0	146	.770	1.91
1294°	100	167	.865	1.44	...	...	...	....
1328°	233	316	1.31	1.77	155	233	.870	1.31
1362°	...	...	....	....	254	317	.979	1.19
1394°	614	631	1.58	3.09	419	397	1.07	1.00
1429°	...	...	....	....	769	610	1.32	1.04
1462°	1,390	1,902	1.68	2.30	1,150	798	1.38	.990
1527°	2,500	2,566	1.54	1.55	1,950	1,102	1.20	.679
1580°	...	...	....	....	2,620	1,500	.973	.427

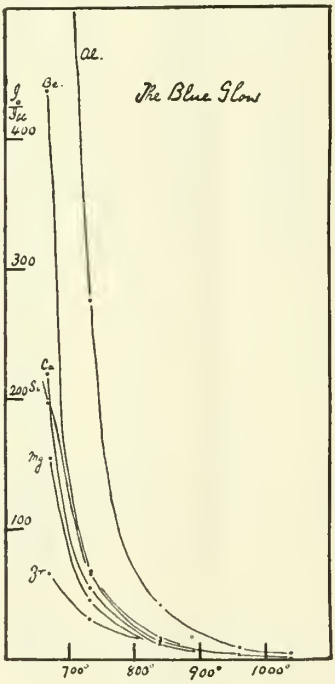


Fig. 3.

The blue glow of six oxides.

determine since it is superimposed upon the spectrum of the temperature-radiation.

It may, however, be discerned under favorable conditions and may be described as lying approximately between .4 μ and .5 μ, but varying as between the various oxides. Estimations for MgO were .48 μ to .42 μ with a maximum at .45 μ, and .45 μ has been taken as the equivalent wave-length.

Fig. 3 shows how the values of I_0/I_{bb} fall off with rising temperatures from the highest readings, which were invariably at the lowest temperature at which it was possible to measure, to values of the order of unity. The curves are approximately exponential. A diagram to this scale indicates nothing of the important outbursts above 1000° where the ratio is small but the actual intensities large, nor does it show the tempera-

ture-radiation of the oxides which for this lower stage of incandescence is too small to appear above the base line.

For temperatures above 1000° we may increase the scale of ordinates

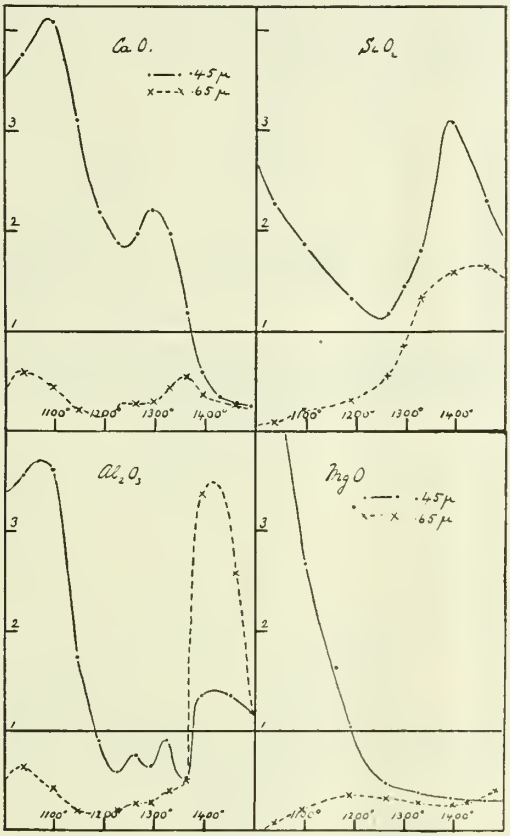


Fig. 4.

Luminescence of CaO, SiO_2, Al_2O_3 and MgO above 1000° C.

as in Figs. 4 to 8 which (except in the case of MgO) display outbursts of luminescence at these higher temperatures.

Table IV.

Outbursts of Luminescence above 1000° in the Oxides given in Tables I., II. and III.

Substance.	Temperatures of Crests.
CaO	1100° and 1300°
Al_2O_3	1075° " 1425°
ZrO_2	1150° " 1450°
SiO_2	1400°
BeO	1225° ....

A discussion of the possible significance of these outbursts will be given in a later paragraph.

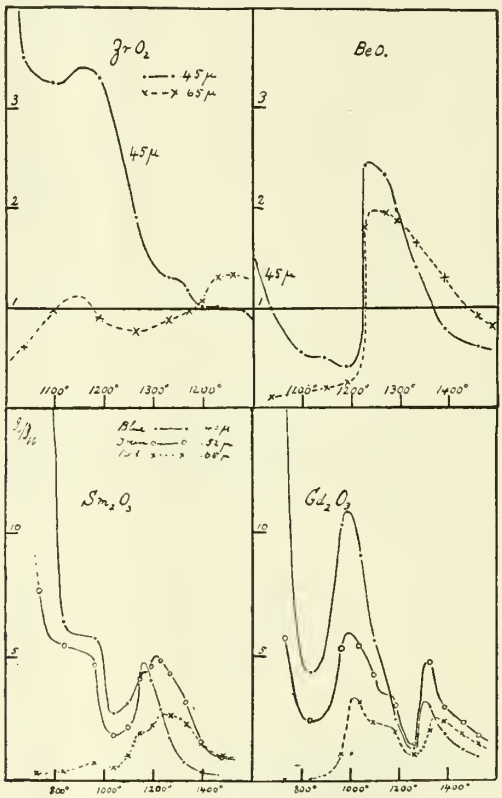


Fig. 5.

Luminescence of ZrO_2, BeO, Sm_2O_3 and Gd_2O_3.

Luminescence of the Incandescent Rare Earths and of the Oxides Erbium and Cerium.

Samarium and gadolinium oxides (Table V. and Fig. 5) have two features in common, as regards their luminescence, with those oxides in which the blue glow occurs.

1. Radiation in the red rises from small relative intensities at the lowest temperatures.

2. The value of I_0/I_{bb} is greatest at the beginnings of incandescence throughout the blue end of the spectrum.

They differ however in that the initial brightness in the green is appreciable at the lowest temperatures and becomes a dominant factor

in the outbursts of luminescence which follow upon the blue glow as the temperature rises.

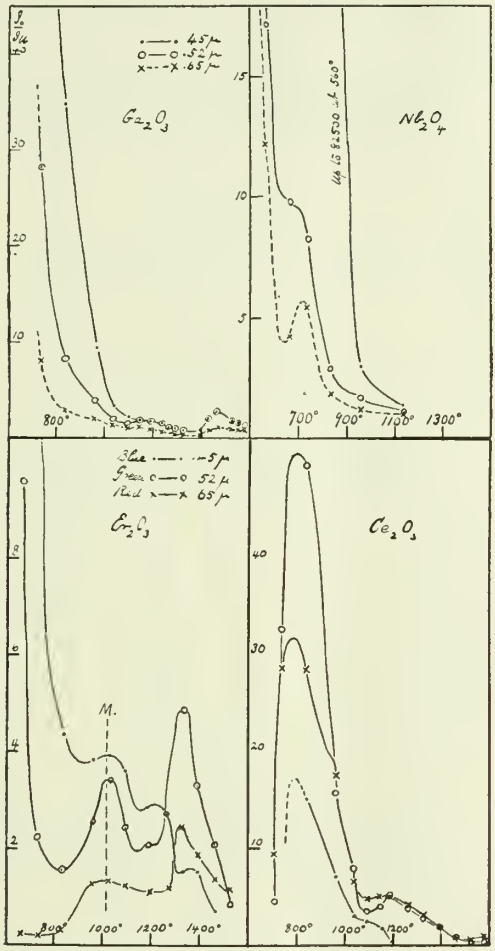


Fig. 6.

Luminescence of Ga_2O_3, Nb_2O_4, Er_2O_3 and Ce_2O_3.

The oxides of gallium and niobium (Table VI. and Fig. 6) represent a further departure in that the largest values of I_0/I_{bb} for the red as well for the green and blue are at the lowest temperatures.

Shortly above 1000° where the niobium oxide was approaching non-selective radiation of an intensity approximately that of a black body, fusion occurred and measurements by our method ended.

This oxide which according to the chemists contained, as is usual, a slight admixture of tantalum oxide, showed by far the brightest lumines-

TABLE V.

Luminescence of Samarium Oxide and of Gadolinium Oxide.

Substance.	Temp. C.	I_o.			I_o/I_{bb}.		
		Red.	Green.	Blue.	Red.	Green.	Blue.
SaO.....	735°	.00049	.0094	.680	.396	7.64	55.1
	837°	.0102	.107	1.55	.425	5.47	6.40
	960°	.314	1.94	2.40	.750	4.64	5.73
	1037°	1.10	3.56	5.31	.563	1.83	2.72
	1097°	6.31	12.9	18.5	1.06	2.18	3.13
	1145°	25.9	55.0	56.0	1.96	4.15	4.23
	1190°	58.9	122	138	2.21	4.60	4.07
	1228°	123	221	132	2.69	4.83	2.88
	1263°	202	331	135	2.63	4.31	1.76
	1328°	417	502	135	2.34	3.16	.750
	1394°	576	611	145	1.48	1.57	.371
	1462°	828	716	271	1.00	.927	.206
GdO.....	735°	.000051	.000708	.0200	.0417	.573	16.2
	837°	.000851	.00596	.108	.0347	.243	4.39
	960°	.447	2.30	5.14	1.067	5.16	12.3
	1037°	5.27	10.6	17.6	3.16	5.43	9.02
	1097°	13.9	25.0	33.4	2.35	4.21	5.64
	1190°	51.2	80.2	66.1	1.93	3.02	2.48
	1263°	78.5	112	97.7	1.02	1.45	1.27
	1328°	230	552	340	1.99	4.79	2.94
	1394°	902	1130	726	2.32	2.91	1.86
	1462°	1556	1902	1092	1.88	2.30	1.32
	1527°	2410	2820	1524	1.48	1.74	0.94

cence below 600° of any of the incandescent oxides included in this series of observations. This permitted readings at 560° at which temperature the intensity through the blue screen was 85200 times that of the same wave lengths from a black body.

In erbium oxide (Table VII. and Fig. 6) we have again the modified blue glow followed at higher stages of incandescence by further outbursts of luminescence.

This substance has been a subject of study since the times of Bunsen on account of the narrow emission bands in its spectrum but it remained for the late W. G. Mallory[1] to show that these bands exceeded the corresponding black-body radiation in intensity.

Mallory explored the visible spectrum through a narrow range of temperature and found a maximum of relative brightness for the red, green and blue regions at about 1000°. The outburst of luminescence at that temperature designated by the vertical line *M*, in Fig. 6 repre-

[1] Mallory, PHYSICAL REVIEW (2), XIV., p. 54.

sents Mallory's effect both as to the approximate temperature and the relative intensity of the red, green and blue regions. His intensities in terms of those of the black body are somewhat larger than ours, which may indicate a more active condition of his luminescent material. It is more likely, however, that working as he did with a spectrophotometer instead of using colored screens, he obtained better defined and more pronounced crests both as to temperature and wave length.

TABLE VI.

Luminescence of Gallium Oxide and Niobium Oxide.

Substance.	Temp. C.	I_o.			I_o/I_{bb}.		
		Red.	Green.	Blue.	Red.	Green.	Blue.
GaO.....	735°	.0100	.0347	.100	8.08	28.1	80.2
	837°	.0733	.209	.851	2.99	8.51	34.7
	960°	.841	1.59	3.94	2.01	3.79	9.40
	1037°	2.60	4.07	6.53	1.32	2.05	3.31
	1097°	6.53	8.51	10.2	1.10	1.43	1.73
	1145°	13.2	22.0	16.8	.995	1.67	1.27
	1190°	26.6	41.7	36.3	1.00	1.57	1.36
	1228°	44.7	63.4	62.4	.978	1.38	1.36
	1263°	53.7	86.1	77.6	.700	1.12	1.01
	1294°	59.6	189	89.1	.515	1.03	.771
	1328°	69.2	155	105	.388	.870	.594
	1394°	143	339	359	.367	.871	.923
	1429°	569	1,097	575	.978	1.87	.988
	1462°	871	2,370	1,097	1.05	2.86	1.325
	1527°	1,679	2,849	2,600	1.03	1.76	1.63
	1555°	2,068	3,350	3,429	.980	1.59	1.62
	1580°	2,341	3,590	4,030	.870	1.33	1.50
NbO.....	560°	.000025	.000035	.174	12.2	17.2	85,200
	665°	.00055	.00126	.277	4.25	9.77	2,150
	735°	.00695	.0100	.398	5.41	8.20	.322
	837°	.0449	.0708	.638	1.83	2.89	26.0
	960°	.513	.692	1.34	1.22	1.65	3.21
	1037°	1.95	2.29	2.66	1.00	1.17	1.35

Mention of this confirmation has already been made in the form of a brief note in *Science*.[1]

Cerium oxide, the luminescence of which is also depicted in Fig. 6, is characterized by the complete absence of blue glow. There is a well-marked outburst at 800° in which the green is dominant and the red about twice as bright as the blue. In a second outburst at 1200° the blue takes no part.

[1] Nichols and Howes, Science, Jan. 13, 1922; p. 53.

The Oxides of Praesodymium and Neodymium.

Through the kindness of Professor James, of New Hampshire College, to whom we owe our samples of the rare earths, we were in possession of a sufficient quantity of these substances, which are rarely to be had in a state of satisfactory separation, to permit of the following observations.

We found the two oxides to differ greatly in their radiating properties.

Table VII.

Luminescence of Erbium Oxide and Cerium Oxide.

Substance.	Temp. C.	I_o.			I_o/I_{bb}.		
		Red.	Green.	Blue.	Red.	Green.	Blue.
ErO.....	665°	.000032	.00136	.00945	.250	10.6	68.4
	735°	.00026	.00278	.0172	.214	2.25	13.9
	837°	.00679	.0389	....	.277	1.58	4.37
	960°	.543	1.07	....	1.29	2.55	3.83
	1037°	2.52	6.61	7.00	1.31	3.39	3.89
	1097°	6.55	14.5	21.4	1.22	2.45	3.61
	1190°	29.9	58.0	76.7	1.12	2.07	2.88
	1263°	130.4	310	207	1.17	2.74	2.69
	1328°	440	871	275	2.47	4.89	1.54
	1394°	725	1,298	745	1.86	3.33	1.55
	1462°	1,148	1,730	575	1.38	2.09	.695
	1527°	1,820	1,413	917	1.12	.870	.565
CeO.....	702°	.0040	.0017	....	8.95	4.72	....
	735°	.0349	.0403	....	28.3	32.6	....
	837°	.692	1.21	.370	28.2	49.5	15.2
	960°	4.92	6.53	3.02	17.7	15.6	7.21
	1037°	13.9	15.3	6.03	7.12	7.85	3.09
	1097°	28.3	21.4	15.1	4.78	3.63	2.55
	1145°	69.5	53.2	25.4	5.25	4.02	1.91
	1190°	133	133	11.7	5.02	5.02	0.44
	1263°	334	304	11.1	4.34	3.95	0.144
	1328°	596	519	25.4	3.34	2.91	.142
	1394°	653	695	87.9	1.58	1.69	.227
	1462°	783	887	113	.950	1.07	.136
	1527°	1,319	1,309	423	.813	.684	.260
	1580°	3,304	1,514	656	1.23	.563	.244

Neodymium oxide at the lower stages of incandescence has several rather narrow well-defined emission bands. These were mentioned by Hartley[1] in 1901 but according to Kayser[2] no study has been made of them.

[1] Hartley and Ramage, Trans. Royal Soc. of Dublin (2), VII., p. 339.

[2] Kayser, Handbuch der Spectroscopie, Bd. VI., Chapter on Neodymium.

A hurried exploration with a hand spectroscope gave as the approximate location of five of these:

$$.660\,\mu;\quad .615\,\mu;\quad .570\,\mu;\quad .550\,\mu;\quad .525\,\mu.$$

At 735° C. the red and green bands were brighter than the corresponding wave lengths in the spectrum of a black body. At 960° the bands were still visible but relatively weak. At 1010° no bands were seen and the radiation was that of a black body both in intensity and distribution. (See Table VIII.)

TABLE VIII.

Luminescence of the Oxides of Praesodymium and Neodymium.

Substance.	Temp. C.	I_0.			I_0/I_{bb}.		
		Red.	Green.	Blue.	Red.	Green.	Blue.
Pr_2O_3.....	665°	.000051	.....	....	.394	....	....
	735°	.00123	.0308	.0254	1.00	2.49	2.00
	837°	.0308	.0468	.0468	1.25	1.91	1.91
	960°	.537	1.76	2.40	1.28	4.20	5.73
	1037°	3.03	7.08	6.22	1.55	3.63	3.19
	1097°	11.5	17.1	8.04	1.94	2.88	1.35
	1145°	26.6	31.6	11.5	2.01	2.39	.870
	1190°	50.4	53.0	43.9	1.90	1.99	1.65
	1228°	85.1	87.7	52.7	1.86	1.92	1.15
	1263°	123	132	51.2	1.61	1.72	.667
	1294°	157	175	52.7	1.35	1.51	.456
	1328°	181	221	71.1	1.00	1.24	.399
	1394°	302	361	126	.744	.929	.324
	1462°	525	659	146	.643	.796	.176
	1527°	877	1,047	367	.541	.646	.135
Nd_2O_3.....	735°	.00243	.00881	....	1.94	7.00	....
	967°	.0871	.204	.348	.152	.417	.712
	1010°	1.12	1.12	1.42	1.00	1.00	1.26

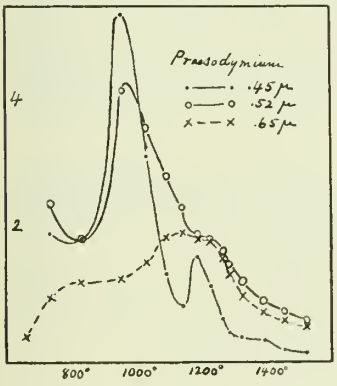


Fig. 7.

Relation of luminescence of ruby and fluorite to that of Al_2O_3 and CaO.

Praesodymium oxide, Pr_2O_3, has a tendency to change into Pr_4O_7 in the oxyhydrogen flame and our observations probably refer to the latter, which is a nearly black powder, or to a mixture of the two oxides.

No narrow bands were visible at any temperature but the continuous spectrum is by no means devoid of luminescence as may be seen from Table VIII. and Fig. 7. There are clearly at least two separate bands, one involving the green and blue and having a moderate

maximum at about 960°, the other in the red with a maximum at about 1150°. The blue glow is absent and above 1300° the blue end of the spectrum is relatively so feeble as to give the incandescent oxide a ruddy hue suggestive of lower temperatures.

SECONDARY FEATURES INDICATIVE OF LUMINESCENCE.

1. *Fatigue.*—The first heating of these oxides to moderate incandescence was frequently found to produce a brightness greatly in excess of that existing after a given temperature had been maintained for some time. The decay, as was to be expected, was very rapid at first and had a diminishing rate. No attempt has been made as yet to determine the curve of decay. A few estimates of the initial brightness of magnesium oxide at a temperature of 1220° gave the following result. Observations were for .45 μ.

$$I_0 = 2690; \qquad I_{bb} = 41.3; \qquad I_0/I_{bb} \doteq 65.3.$$

The usual value at this temperature after ignition for several minutes was less than unity (see Fig. 4). The above readings were made about 0.3 second after ignition and are doubtless too late for the actual maximum.

This fatigue has long been known in the case of lime cylinders against which an oxy-hydrogen flame impinges and decay curves were made many years ago.[1]

Probably the limiting value for initial brightness is obtained when we burn a metal like magnesium. W. H. Pickering[2], long before the general laws of radiation had been developed, estimated the temperature corresponding to the spectral distribution of the light from the magnesium flame at 4900° C. It is now easy to check his value which was based upon a purely empirical relation between the ratio of red and blue in the spectrum and the temperature by applying the distribution law to the spectrum of this flame. The result gives about 5000° C. and since the actual temperature of the flame, as studied by F. J. Rogers,[3] cannot be above 2000°, this means that 98% or more of the light must be ascribed to luminescence.[4]

2. *Effects of Heat Treatment.*—As in the preparation of phosphorescent substances for excitation by light or by kathode rays, so here the effects of previous heat treatment are varied and complicated.

In some cases the previous heating of an oxide to full incandescence

[1] Nichols and Crehore, PHYSICAL REVIEW (1), II., p. 161.

[2] W. H. Pickering, Proc. Am. Acad. of Arts and Sciences. 1879–80, p. 236.

[3] F. J. Rogers, Am. J. of Sc., XLIII, p. 301, 1892.

[4] Nichols, Trans. Ill. Eng. Soc., Oct. 10, 1921.

seems to be essential to the blue glow and to other luminescent outbursts belonging to the lower stages (below 1000°). Sometimes, however, heating to moderate temperatures reduces the glow. A sample of beryllium oxide not previously ignited was heated in the H-O flame to about 1000° and after a fairly stable state had been reached was allowed to cool, stepwise, by gradually reducing the flame. In this way the

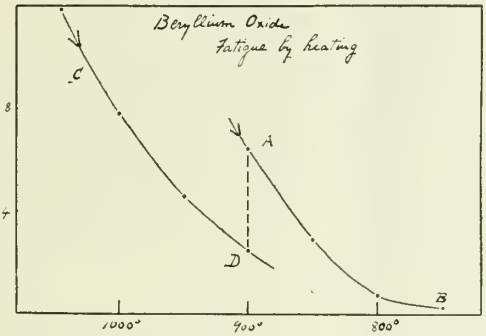


Fig. 8.

Effect of fatigue by heating.

upper curve in Fig. 8 was obtained. The temperature was then increased to about 1300°. The lower curve indicates the brightness on cooling after this treatment.

Heating to incipient fusion, *i.e.*, until the surface of the oxide became mobile as observed with the pyrometer, had in one instance a more striking result.

A sample of aluminum oxide which showed the blue glow and which on further heating step by step developed the usual outbursts at (1000°–1100°) and (1300°–1500°), showed signs of fusion. On cooling stepwise in the flame the outburst at (1300°–1500°) was repeated but of the luminescence at lower temperatures all but a trace was gone. The intensity at 735° as viewed through the blue screen was now I_0/I_{bb} = 1.02 instead of the previous value of 67.3.

3. *Influence of the Mode of Heating.*—The type of luminescence now under consideration, unlike the luminescence by flame excitation recently described,[1] is not confined to substances exposed to the action of the hydrogen flame. It is for example possible to see the blue glow when beryllium oxide is heated in a crucible, or when zinc oxide or other oxides are electrically heated on a strip of platinum foil. The effect is however much more intense when the flame is used, and the brightness is greatly affected by changes in the supply of oxygen so slight that the actual

[1] Nichols and Wilber, Physical Review (2), XVII., p. 453.

temperature, as indicated by the radiation from the black surface, is not appreciably modified.

The following observations upon magnesium oxide using adjustments of hydrogen and oxygen such as to maintain a constant temperature may serve to illustrate this point.

MgO. Temperature 1220° C.; $I_{bb} = 41.3$.

With excess of hydrogen: $I_0 = 57.0$; $I_0/I_{bb} = 1.38$.

With excess of oxygen: $I_0 = 151$; $I_0/I_{bb} = 3.66$.

The general luminescent activity of the oxide was somewhat greater than in the foregoing experiment on fatigue.

It was noted in the course of these trials that the sensitiveness to oxygen seemed to differ with the various oxides and for a given oxide was much greater at some temperatures than at others. This presumably depends on whether the observation is made at a temperature corresponding to one of the outbursts of luminescence.

This is a point not yet definitely established by systematic experiments with several different oxides. It was noted however in the course of our measurements with praesodymium oxide that this substance was exceedingly sensitive to the slightest changes in the supply of oxygen at temperatures around 1000°. Above 1300° where there is little but temperature radiation in evidence this sensitiveness had disappeared.

The Effects of Admixture.

That the photo-luminescence of various sulphides and oxides is due to the presence of certain activating substances and that the kathodo-luminescence of the oxides with which we are concerned is profoundly modified by the minutest traces of the same, has long been known. It was of interest therefore to note the effect of such admixtures upon the luminescence of the incandescent oxides. Two such preparations were at hand with which to make the test.

1. A sample of aluminum oxide heated to 1200° with 2 per cent. of a chromium salt as in the making of synthetic rubies (a finely phosphorescent preparation due to Mr. W. C. Andrews).

2. A crystal of fluorite showing in the kathode tube the narrow line-like bands ascribed to the presence of rare earths. (This was one of the specimens then under spectroscopic observation by Miss Frances G. Wick.)

When incandescent these exhibited the rather complicated series of outbursts shown in Fig. 9. A comparison with the results obtained with Al_2O_3 and CaO respectively show that the luminescence of these oxides forms a component but only a minor part of the display. To render

such a comparison visually easy, the luminescence as seen through a single screen is plotted for Al_2O_3 and the ruby and for CaO and the fluorite in the same diagram.

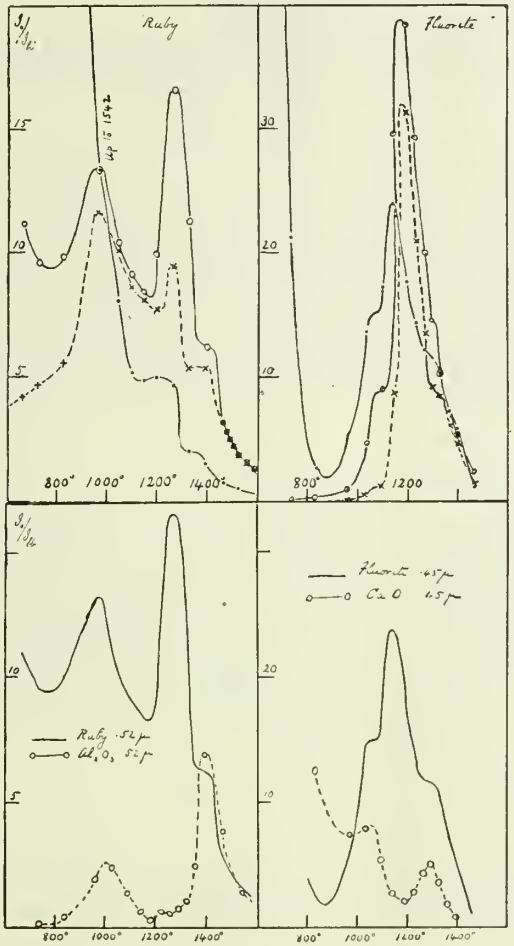


Fig. 9.

Luminescence of praesodymium oxide.

Whether all luminescence within the incandescent range is due to activating admixtures would perhaps be as difficult of positive determination as in the vexed case of kathodo-luminescence. Thus far we have been unable to procure or produce oxides of a purity such that they would not respond to the excitation of kathode-bombardment. Neither have we found any which fail of luminescence when incandescent.

LUMINESCENCE A PHENOMENON OF INSTABILITY.

There is abundant evidence to connect the luminescent glow of these incandescent oxides, between definite temperature limits, with changes in the physical properties of the substance.

That the luminescence of zinc oxide is coincident as to temperature with changes in the electrical resistance and its allied properties has already been pointed out.[1] All the oxides which show the blue glow[2] are known to be going through the change from infinite resistance to low resistance within the range of temperatures through which the glow persists. The outburst manifested by aluminum oxide at (1000°–1100°) occurs where the resistivity curves of Northrup[3] for alundum show an inflection and the more pronounced luminescence of that oxide between 1300° and 1500° coincides with similar irregularities in the relations between temperature and resistivity published by Hering[4] from Northrup's data. Finally the display of luminescence by silica between 1300° and 1500° (see Fig. 4), finds its counterpart in the well-established transformation point of quartz.

It is as though during such rearrangements in the structure, the light-producing process which we term luminescence can go on, a concept which brings the effects here considered into a certain relationship to the views recently urged by Perrin and supported by R. W. Wood. If the light-producing process is an oxidation, following and alternating with partial breakings down, degenerations or reductions under the influence of temperature, the luminescence of incandescent oxides must be regarded as akin to those other types of luminescence for which oxidation is already the established and accepted cause.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY,
November 25, 1921.

[1] Nichols, PHYSICAL REVIEW (2), XVII., p. 430.

[2] Nichols and Howes, Journal of the Optical Society of America, VI., No. 1, 1922.

[3] E. F. Northrup, Metallurgical and Chem. Eng., XII., p. 125, 1914.

[4] C. Hering, Metallurgical and Chem. Eng., XIII., p. 25, 1915.

THE DIELECTRIC CONSTANT OF MICA.

By J. R. Weeks, Jr.

Synopsis.

Dielectric Constant of Mica.—The constant was determined for 18 samples of mica, varying in thickness from 0.005 to 0.073 inch and including 12 different grades. Each sheet was placed between two mercury electrodes and the capacity of the condenser thus formed was determined with a shielded capacity and conductance bridge using alternating current at 1,000 cycles per second. It was found that while thick sheets with plainly visible air films had low dielectric constants, those without such films gave fairly consistent results, running from 6.4 to 9.3 with an average of 8.1. When a thick sheet was split, the thinner sheets had higher constants except in the case of a sample of Canadian amber.

Power Loss in Mica Condensers was too small to determine accurately with the apparatus used, but was higher for stained than for clear micas.

In looking for an average value of the dielectric constant of mica in the handbooks of the Physical Constants of materials such as, the Smithsonian Tables, Kays and Laby, Chemiker Kalender, and Landolt-Börnstein, the writer was impressed with the wide variations found by different investigators. The values given in these reference books varied from 2.5 to 10. It seemed likely that at least a part of this large variation might be due to air pockets or films between the various laminæ, especially since most of these low values were found on rather thick sheets. The high values, on the other hand, might be due to conducting films between the laminæ increasing the effective area of the electrodes. Therefore, it was decided to measure the dielectric constant of different grades of mica, and especially those grades used by other investigators, with a view of making an accurate determination of the dielectric constant and of finding, if possible, the causes of these wide variations.

Accordingly 18 samples of mica of varying thicknesses were obtained, including 12 different grades. Unfortunately it was impossible to obtain all of the grades for which other investigators had given low values. These grades apparently do not reach the New York market (India micas). It was possible, however, to get mica of the same thicknesses as were used in these other investigations. The samples were numbered from 1 to 18. The subscripts A, B and C denote thin sheets split from the original sheet after the first measurement was made.

METHOD.

Most of the sheets did not require cutting, but where necessary the sheet was clamped between brass plates and carefully cut to $3\frac{1}{4} \times 2\frac{1}{2}$ inches with a sharp knife. The sheet of mica was floated upon a copper plate amalgamated with mercury which served as the bottom electrode. This plate was grounded. The top electrode consisted of a hollow brass rectangle $1\frac{7}{8} \times 2\frac{5}{8} \times \frac{1}{4}$ inches high. This rectangle was placed in the center of the sample and filled with mercury.

The capacity of the condenser thus formed was measured with alternating current at 1,000 cycles per second by a shielded [1] capacity and conductance bridge which had been checked against condensers calibrated by the Bureau of Standards. The thickness of the sheet between the electrodes was measured with an accurate micrometer, measuring to 0.0001 inch. Wherever the original sheet was thick enough, it was split into thinner sheets along its natural lines of cleavage and each of these measured as above. Considerable difficulty was experienced in preventing air pockets from forming between the mercury and the sheet on the under side. Every effort was made to reduce to a minimum the errors introduced by these air pockets and in each case the highest obtainable capacity reading was taken as the correct one. The individual capacities varied from 100 to 1,200 mmf. Over this range of capacity the bridge error was less than 1 per cent.

The results of these measurements are given in Table I. There is a probable error not greater than minus 5 per cent. due to air films between the electrodes and the sheet. Check readings given for samples of Madras green 5–*A* and 5–*B* show how closely it was possible to duplicate readings. The sample 5 having a dielectric constant of 2.9, was very badly split and the various laminæ were quite noticeably separated. However, thin sheets split from this sample had dielectric constants of 6.6 to 8.4. It was this effect, namely a thick sheet having a low dielectric constant (due to air films) while thin sheets split from it had a high dielectric constant, which undoubtedly caused the low values given by others. Sample 17 further illustrates the above point. It had a dielectric constant of 4.8 while thin sheets split from it had dielectric constants of 8.4 and 8.6.

While some sheets having plainly visible stains did have a dielectric constant somewhat higher than the average, there was no such pronounced effect as that shown by air films. None of the sheets, however, was badly stained. Sheets 7, 8 and 9 were the only ones having stains

[1] G. A. Campbell, Elect. World and Eng., Vol. XLIII, pp. 647, 1904.

which looked at all like continuous films. These sheets had dielectric constants a little higher than the average value of 8.1.

TABLE I.

Sample.	Thickness Inches.	Dielectric Constant.	Material.
1	.0273	7.9	Madras brown
1-*A*	.0134	7.9	" "
1-*B*	.0143	8.4	" "
2	.0165	8.7	" "
3	.0218	8.7	Madras ruby
4	.0534	8.1	Canadian amber
4-*A*	.0270	8.0	" "
4-*B*	.0142	7.3	" "
4-*C*	.0071	6.4	" "
5	.0274	2.9	Madras green
5-*A*	.0045	7.0(6.6)	" "
5-*B*	.0048	8.0(7.9)	" "
5-*C*	.0064	8.4	" "
6	.0232	8.0	" "
7	.0122	9.3	Indian brown stained
8	.0052	8.4	" " "
9	.0065	8.9	" " "
10	.0060	8.6	Ruby—source unknown
11	.0031	7.2	Clear—source unknown
12	.0286	8.1	Argentine clear
12-*A*	.0076	8.0	" "
13	.0294	7.4	Brazilian stained
13-*A*	.0104	8.1	" "
13-*B*	.0190	8.2	" "
14	.0158	8.6	Brazilian clear
15	.0643	6.6	Argentine stained
15-*A*	.0113	8.0	" "
15-*B*	.0117	5.9	" "
15-*C*	.0068	7.7	" "
16	.0674	5.6	Indian brown clear
17	.0736	4.8	" " "
17-*A*	.0122	8.6	" " "
17-*B*	.0097	8.4	" " "
18	.0233	8.4	Argentine clear
18-*A*	.0088	8.8	" "

Samples 5, 15-B, 16 and 17 had visible air films.
Samples without visible air films—Average 8.1
Maximum 9.3
Minimum 6.4

The phase angle also was measured, but the bridge readings were too small to make an accurate determination possible. The phase angle readings showed that stained sheets had higher losses than clear sheets.

CONCLUSIONS.

1. When air films in the interior of the sample of mica were eliminated by splitting it along its natural lines of cleavage into thin sheets, in no case was the dielectric constant less than 6.4.

2. Where air films were plainly visible, the dielectric constant was low (2.9 to 4.8).

3. It seems likely that the low values given by some investigators undoubtedly were due to air films between the laminæ. These air films were in most cases very hard to see without carefully examining the edges of the sheets.

4. Stained sheets did not show a dielectric constant enough higher than the average value of 8.1 to determine the effect of stains in mica upon the dielectric constant.

5. No difference in the dielectric constant is readily discernible between the different grades or kinds of mica which were tested.

RESEARCH LABORATORIES OF THE
AMERICAN TELEPHONE AND TELEGRAPH COMPANY
AND WESTERN ELECTRIC COMPANY, INC.

A NEW GYROSCOPIC CONSTRUCTION IN SIMPLE VECTORS.

By Will C. Baker.

Synopsis.

Simple Vector Representation of the Steady Precession of a Gyroscope.—By means of vector angular momentum diagrams, the quadratic for steady precession is derived graphically, and the variation in the steady precession at constant angle with change of applied couple is represented so as to be easily visualized. The couple required to prevent precession due to the earth's rotation is also given in a vector diagram.

In all cases of the free precession of a rotating body, the looped or oscillatory path of the axis is an essential part of the motion. Yet, whenever the angular momentum of spin is high enough, these oscillations become vanishingly small. As most of the cases of interest to the average student are of this type, *i.e.*, the approximately steady precession, the following geometrical constructions are of interest.

Following the usual plan, resolve the precessional velocity, $\dot{\psi}$, into (1) a compoment $\dot{\psi}\cos\theta$ about OC (Fig. 1, *a* and *b*) and (2) $\dot{\psi}\sin\theta$ about OE. Take C, A, A, as the moments of inertia of the top about the axes OC, OE, OD, and let ω be the angular velocity of spin about OC. Thus the components of angular momentum are $C(\omega + \dot{\psi}\cos\theta)$, or Cn, about OC and $A\dot{\psi}\sin\theta$ about OE. Represent these at a given instant by the vector diagram of Fig. 2 in which $OS = Cn$, and $SQ = A\dot{\psi}\sin\theta$. Thus

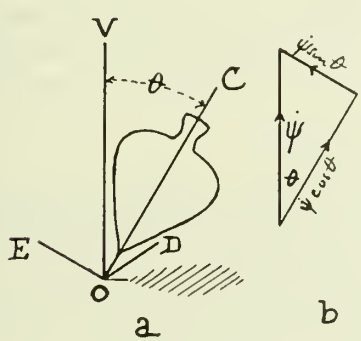


Fig. 1.

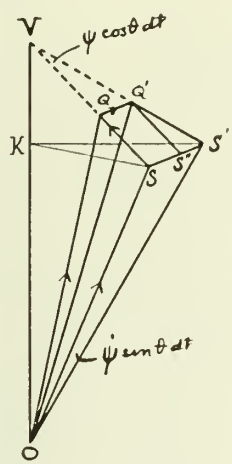


Fig. 2.

OQ is the resultant angular momentum at the instant when OS is parallel to the axis of the top. Now, instead of attacking this plane figure, $OVQS$, algebraically as in the well-known construction of Sir George Greenhill,[1] let us represent on the same diagram (in three dimensions) the position of these vectors after the lapse of a small time dt.[2] The plane defined by OSV will have rotated through the small angle $\dot{\psi}dt$ (given by SKS' on the figure, and as the final angular momentum OQ' is equal to the initial value OQ plus the vector QQ', the latter must be the angular impulse $(Mgh \sin \theta)dt$, received by the system during the interval. Here M is the mass, and h the distance from the pivot to the center of mass of the top. Thus we have:

$$\begin{aligned} QQ' &= Mgh \sin \theta dt, \\ OS &= OS' = Cn, \\ SQ &= S'Q' = A\dot{\psi} \sin \theta, \\ &\angle SKS' = \dot{\psi}dt, \\ &\angle SVS' = \dot{\psi}dt \cos \theta, \\ &\angle SOS' = \dot{\psi}dt \sin \theta. \end{aligned}$$

Also if $Q'S''$ be drawn parallel to QS,

$$\begin{aligned} SS' = SS'' + S''S' &= QQ' + Q'S' \sin S'Q'S''. \\ &= (Mgh \sin \theta)dt + (A\dot{\psi} \sin \theta)(\dot{\psi} \cos \theta dt). \end{aligned}$$

But $SS' = OS \angle SOS' = Cn\dot{\psi} \sin \theta dt$.

Whence, equating the two values of SS', and cancelling the common factors we find

$$(Cn - A\dot{\psi} \cos \theta)\dot{\psi} = Mgh,$$

the well-known quadratic for steady precession, usually obtained in less simple ways.

Consider now the relations involved in the elementary triangles VQQ' and VSS' remembering that the angles at V are all infinitesimal; and make a new diagram (Fig. 3, a and b) in which the plane of these figures is the plane of the paper, the same letters being used for the same points

[1] Greenhill, Notes on Dynamics. Greenhill, Report on Gyroscopic Theory, Chap. I., §§ 3 et sqq. Gray and Gray, Treatise on Dynamics, § 271.

[2] Some have condemned this use of the element of time dt, apparently on the ground that, as the motion is strictly oscillatory, the value of θ must, in general, change during this time. Perhaps these writers would consent to the employment of the symbol Δt with the proviso that it denote an integral number of the periods of the motion. This would still be a small time as the period is very short in the cases to which the above considerations are applicable. The vectors representing the change in the angular momentum still give the integral impulse over the time taken. This surely is an unnecessary refinement, for when the precession is approximately steady the period is very small and the amplitude negligible.

as in Fig. 2. Take A as the mid point of VS, and denote the distance AQ by x and VS by L

$$QQ' = VQ \angle QVQ' = (VA + AQ) \angle QVQ'$$

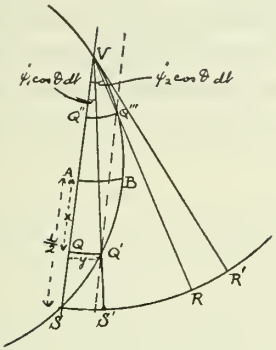


Fig. 3, *a*.

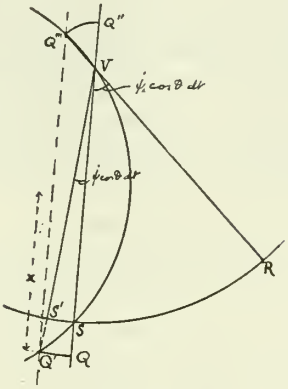


Fig. 3, *b*.

$$= \left(\frac{L}{2} + x\right)(\dot{\psi} \cos \theta dt)$$

$$= (Mgh \sin \theta)dt, \text{ as before.}$$

Hence

$$\left(\frac{L}{2} + x\right)(\dot{\psi} \cos \theta) = Mgh \sin \theta \tag{1}$$

Also

$$QS = \left(\frac{L}{2} - x\right) = A\dot{\psi} \sin \theta \tag{2}$$

From these, by multiplication,

$$\frac{L^2}{4} - x^2 \doteq AMgh \tan \theta \sin \theta \tag{3}$$

$$= A \tan \theta \frac{QQ'}{dt}.$$

Hence

$$\frac{QQ'}{dt} = y = \frac{\frac{L^2}{4} - x^2}{A \tan \theta}.$$

Or, substituting (see Fig. 2) $L = Cn \tan \theta$,

$$\frac{C^2n^2 \tan \theta}{4A} - y = \frac{x^2}{A \tan \theta}.$$

In view of the fact that, due to the short time dt, the arcs QQ', etc., may

be treated as short straight lines perpendicular to VS, this equation exhibits the locus of Q', for constant θ, as a parabola passing through the points V and S, with its vertex opposite A, ($x = 0$) at a distance ($C^2n^2 \tan \theta/4A$). Thus for a given value of the applied couple ($Mgh \sin \theta$, represented by the distance of the dotted line from VS) we find two solutions corresponding to the two points common to the curve and the dotted line. These give the two possible steady precessions at angle θ for the same applied couple; $\dot{\psi}_1$ proportional to the angle SVS', and $\dot{\psi}_2$ proportional to the angle SVR, as either of these angles is swept out in the same small time dt.

Further it is obvious, from the nature of the curve, that an increase in the applied couple brings both Q' and Q''' towards the vertex B, increasing the lower value of the precession, *i.e.*, increasing the angle SVS', and decreasing the value of the higher precession, *i.e.*, decreasing the angle SVR. With still greater increase in the applied couple these points (Q', Q''') finally meet at the vertex B for which condition, by putting x equal to zero in equation 1 we find the limiting value

$$Mgh \sin \theta_{x=0} = \frac{L}{2} \dot{\psi} \cos \theta ,$$

or inserting $L = VS = Cn \tan \theta$. (See Fig. 1.)

$$= \frac{Cn}{2} \dot{\psi} \tan \theta, \cos \theta.$$

Or from equation 3 in the same way

$$Mgh \sin \theta_{x=0} = \frac{C^2n^2 \tan \theta}{4A} .$$

For values of the applied couple greater than this there is obviously no real solution and therefore no possible value for *steady* precession.

Now, following the changes in the opposite direction (of decreasing values of the applied couple) we are led, for zero couple, to zero precession for the lower value (Q' coinciding with S) and for the upper value (Q''' coinciding with V) to a precession given by

$$\dot{\psi}_V = \frac{\angle SVR'}{\cos \theta dt}$$

(VR' being tangent to the curve at V) which is the free precession of Euler or the adynamic precession of Kelvin.

If the applied couple now becomes negative (Fig. 3*b*) we deal with points on the curve below S and above V. The lower precession changes

sign, having passed through zero, while the upper one continues to increase, having passed through the adynamic value.

From these characteristics of the change of the precession with change in the applied couple, the rise or fall of the axis of the top with a forced change in the magnitude of the free precession, follows in the usual way.

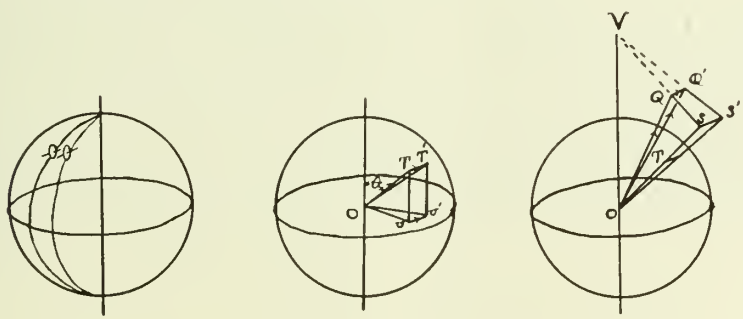
There is another way of indicating these changes, which while it gives a less vivid picture of the relations between them, yet gives exact values in place of the merely relative values of the other method. One notes from equation 2 that SQ and SQ'' represent the two values of $A\dot{\psi} \sin \theta$. Thus

$$\dot{\psi}_1 = \frac{SQ}{A \sin \theta}$$

and

$$\dot{\psi}_2 = \frac{SQ''}{A \sin \theta},$$

so the values of the two precessions are given by the distances of Q and Q'' from S, whether these be positive or negative (*i.e.*, whether these points fall between S and V or are external to that segment. Further we see that since $x = AQ = AQ''$ that the sum of $SQ + SQ''$ is always SV, *i.e.*, the sum of the two velocities for steady precession is always that of the free or adynamic precession, $Cn/(A \cos \theta)$.



a c b

Fig. 4.

In the case of a rotating body in precession along a predetermined path, as, for instance, a flywheel with axis fixed with regard to a rotating earth, the general construction is the same. We should have a position diagram (Fig. 4, *a*) showing the positions of the rotating body at an interval of dt. Then the vector diagram (Fig. 4, *b*) where all points are lettered to correspond to those of Fig. 1, and where θ is the angle between the axes of the earth and of the flywheel. QQ' is the angular impulse required to change the resultant angular momentum OQ to the value

(OQ') it has dt later and the calculation follows as before. However as the angular velocity of the earth about its axis, $\dot{\psi}_e$ is so very small with respect to ω in the cases of chief interest (effort of flywheel to precess, couple on gyro-compass, etc.) the vectors TS and SQ, *i.e.*, $C\dot{\psi}_e \cos\theta$ and $A\dot{\psi}_e \sin\theta$, are ignored and the figure becomes that of Fig. 4 *c*, where $OT = OT' = C\omega$ and TT' (or UU') is the impulse $(C\omega \sin\theta\dot{\psi}_e)dt$. Hence the couple required to prevent precession towards the pole of the earth is $C\omega\dot{\psi}_e \sin\theta$; the result usually obtained by more complex analysis. The couple on a gyro-compass is simply the vertical component of this couple at the place in question.

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KINGSTON, ONT.,
September 5, 1921.

THE PATH OF A RIGID ELECTRON WHICH MOVES IN A MAGNETIC FIELD OF CONSTANT STRENGTH ROTATING WITH CONSTANT ANGULAR VELOCITY.

By E. O. Hulburt.

Synopsis.

Equations of Motion of a Rigid Electron in a Uniformly Rotating Magnetic Field of constant strength rotating with a frequency $\omega/2\pi$ in the XZ plane, are obtained. The reactions on the motion due to finite size, radiation, and the variation of mass with velocity are neglected. If initially the velocity of the electron has components only along the X-axis or the Z-axis the path of the electron is a wavy curve inside an annular space whose axis is parallel to the Y-axis. If the initial velocity of the electron has components only along the Y-axis the path is a rather complicated type of spiral winding in the general direction of the Y-axis. It is found that a high frequency of rotation of the magnetic field, of the order of 10^6, such as may be produced by means of electron-tube circuits, would not impart a great velocity to the electron.

1. A rigid electron is assumed of mass m and charge e and of size small in comparison with the displacements it undergoes. The electron is subjected to a magnetic field whose components are H_x, H_y and H_z. The reactions on its motion due to the variation of mass with velocity and to radiation both from the electron and from the magnetic field are neglected. Let x, y and z be the positional coördinates of the electron. When electromagnetic units are used, the equations of motion of the electron are, in Newtonian notation,

$$\begin{aligned} \frac{m}{e}\ddot{x} &= H_y\dot{z} - H_z\dot{y}, \\ \frac{m}{e}\ddot{y} &= H_z\dot{x} - H_x\dot{z}, \\ \frac{m}{e}\ddot{z} &= H_x\dot{y} - H_y\dot{x}. \end{aligned} \tag{1}$$

Let H rotate in the XZ plane with a constant angular velocity of frequency $\omega/2\pi$. Then

$$H_x = H\cos\omega t, \qquad H_y = 0, \qquad H_z = H\sin\omega t. \tag{2}$$

Introducing (2) into (1) gives

$$\begin{aligned} \frac{m}{e}\ddot{x} &= -H\dot{y}\sin\omega t, \\ \frac{m}{e}\ddot{y} &= H(\dot{x}\sin\omega t - \dot{z}\cos\omega t), \\ \frac{m}{e}\ddot{z} &= H\dot{y}\cos\omega t. \end{aligned} \tag{3}$$

These equations may be integrated and the constants of integration determined from the initial conditions.

2. Suppose initially that when $t = 0$, $x = y = z = \dot{x} = \dot{y} = 0$ and $\dot{z} = w$. The solutions[1] of (3) are in this case,

$$\begin{aligned} x &= \frac{wH^2e^2}{2\nu m^2}\left[\frac{\cos(\nu+\omega)t}{(\nu+\omega)^2} - \frac{\cos(\nu-\omega)t}{(\nu-\omega)^2}\right] + \frac{2\omega w m^2}{H^2e^2}, \\ y &= \frac{wHe}{\nu^2 m}[\cos\nu t - 1], \\ z &= \frac{wH^2e^2}{2\nu m^2}\left[\frac{\sin(\nu+\omega)t}{(\nu+\omega)^2} + \frac{\sin(\nu-\omega)t}{(\nu-\omega)^2}\right], \end{aligned} \tag{4}$$

where

$$\nu = \sqrt{\frac{H^2e^2}{m^2} + \omega^2}.$$

To reduce to the case of a stationary magnetic field, ω is placed equal to zero in (2) and (4). Then $\nu = He/m$, $H_x = H$, $H_y = H_z = 0$, and (4) becomes

$$\begin{aligned} x &= 0, \\ y &= \frac{wm}{He}\left(\cos\frac{He}{m}t - 1\right), \\ z &= \frac{wm}{He}\sin\frac{He}{m}t. \end{aligned} \tag{5}$$

We see from (5) that the electron moves in a circle in the YZ plane of radius wm/He and with the centre at $(0, -wm/He, 0)$. This is in agreement with formulas given by others.[2]

3. The determination of the path of the electron from equations (4) is facilitated by noticing that

$$\sqrt{\left(x - \frac{2\omega w m^2}{H^2e^2}\right) + z^2} = \frac{wH^2e^2}{2\nu m^2}\sqrt{\frac{1}{(\nu+\omega)^4} + \frac{1}{(\nu-\omega)^4} - \frac{2\cos\nu t}{(\nu^2-\omega^2)^2}}. \tag{6}$$

[1] I am indebted to Dr. E. W. Chittenden of the Mathematics Department for these solutions.

[2] J. J. Thomson, Conduction of Electricity through Gases, page 107, 1906.

This transformed to polar coördinates is

$$\rho = \sqrt{a + b \cos 2\nu t}, \tag{7}$$

where ρ, a and b are determined by identifying (7) with (6). From (7) it follows that at no time does ρ become greater than $\sqrt{a + b}$ or less than $\sqrt{a - b}$. Hence the electron moves always between two coaxial cylindrical surfaces of radii $\sqrt{a + b}$ and $\sqrt{a - b}$, the axis of the surfaces being parallel to the Y-axis. The equation of the axis is

$$x = \frac{2\omega w m^2}{H^2 e^2},$$

$$z = 0.$$

Further, from (4) it is seen that y varies harmonically with the time reaching the extreme values 0 and $-2\omega \times He/\nu^2 m$. Therefore the electron moves always between the two planes $y = 0$ and $y = -2\omega He/\nu^2 m$. With these facts in mind it is found that the electron pursues a wavy orbit inside the annular space as indicated in Fig. 1. The electron does not in general retrace its path during its subsequent excursion through the space to which it is confined.

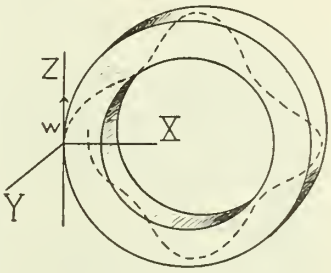


Fig. 1.

The case in which the electron has initial velocity components only along the X-axis is by symmetry the same as the case just discussed, and the path of the electron is of the same form as that of Fig. 1.

4. If the initial conditions are $t = 0$,

$$x = y = z = \dot{x} = \dot{z} = 0, \text{ and } \dot{y} = v,$$

the solutions of (4) are:

$$x = \frac{vH^3e^3}{2\nu^2m^3}\left[\frac{\sin(\nu + \omega)t}{(\nu + \omega)^2} - \frac{\sin(\nu - \omega)t}{(\nu - \omega)^2}\right] + \frac{vHe}{\nu^2 m}\sin \omega t,$$

$$y = \frac{vH^2e^2}{\nu^3m^2}\sin \nu t + \frac{v\omega^2}{\nu^2}t, \tag{8}$$

$$z = -\frac{vH^3e^3}{2\nu^2m^3}\left[\frac{\cos(\nu + \omega)t}{(\nu + \omega)^2} + \frac{\cos(\nu - \omega)t}{(\nu - \omega)^2}\right] - \frac{vHe}{\nu^2 m}\cos \omega t + \frac{2vm}{He}.$$

The path of the electron is found by transforming equations (8) to a new set of axes X', Y', Z', such that the new coördinates x', y', z', are

related to the old ones x, y, z by the relations

$$x' = x - \frac{vHe}{\nu^2 m} \sin \omega t,$$

$$y' = y - \frac{v\omega^2}{\nu^2} t,$$

$$z' = z + \frac{vHe}{\nu^2 m} \cos \omega t - \frac{2vm}{He}.$$

The new axes remain always respectively parallel to the old ones. The new origin moves on a spiral wound on a cylinder, circumventing the cylinder $\omega/2\pi$ times a second and advancing with a velocity whose Y-component is $v\omega^2/\nu^2$. The radius of the cylinder is $vHe/\nu^2 m$; the equation of its axis is

$$x = 0,$$

$$z = \frac{2vm}{He}.$$

With reference to the new axes the path of the electron is of the same form as discussed in section (3). With reference to the old axes the path is a rather complicated type of spiral winding in the general direction of the Y-axis.

5. A special case occurs when ω is large. This is of interest because it is possible by means of electron tube circuits to produce magnetic fields which rotate with frequencies of the order of 10^6, although with the apparatus available at present such fields are relatively weak. If ω is large and if the initial conditions are those of section (2) we find that y, z, $\dot{x}$, $\dot{y}$, $\dot{z}$ are small and x is large. With the initial conditions of (3) and with ω large, x, z, $\dot{x}$, $\dot{z}$ are small, $y \doteq vt$ and $\dot{y} \doteq v$. We see from this that even when the magnetic field rotates at a high frequency the electron does not acquire a very great velocity.

STATE UNIVERSITY OF IOWA,
November, 1921.

THE THERMOPHONE.

By Edward C. Wente.

Synopsis.

Acoustic Efficiency of Thermophones of the Heated Foil or Wire Type.—Theoretical formulæ are derived for the maximum value of the alternating pressure produced within the enclosure of any thermophone when a given alternating current, superposed on a direct current, is passed through the central foil or wire. The effect of certain simplifying assumptions which are made is shown to be small in practical cases. As an *experimental verification* of the formulæ, an electrostatic transmitter was calibrated for a wide range of frequencies with four thermophones which differed greatly in their physical constants, the formulæ being used to compute the pressures produced. The four calibrations thus obtained agree with each other closely and also with an independent calibration made with a pistonphone.

Methods of Calibrating Acoustical Transmitters.—In addition to the pistonphone, the thermophone is now available. The circuits used in calibrating an electrostatic transmitter are given.

Method of Measuring the Thermal Conductivity of a Gas by Using a Thermophone is Suggested.—It would have the advantage of avoiding difficulties due to convection.

In a paper on the theory of the thermophone, Arnold and Crandall[1] have developed formulæ for the absolute value of its acoustical efficiency as a function of the frequency. While these formulæ are sufficiently accurate for most practical purposes, certain discrepancies[2] have been observed, which cannot be attributed to experimental errors. In order to use the thermophone for calibrating acoustical apparatus throughout a wide range of frequencies it has therefore been necessary to make a more detailed analysis of its action.

In this paper formulæ are derived for the efficiency of a thermophone with a heating element of metal foil, which are found to agree closely with such experimental tests as it has been possible to apply. Expressions for the efficiency of the thermophone having a wire heating element are also obtained by the same method of analysis. Only those cases are considered in which the thermophone heating element is located within an enclosure the linear dimensions of which are small in comparison with the wave length of sound. When the element is not placed within a small enclosure the thermophone is of little importance as a precision instrument. Its sound output is not only small but indefinite in most practical cases. Since the sound waves are generated by the alternate expansion and contraction of a layer of air in the immediate

[1] Phys. Rev., X, 22 (1917).

[2] Phys. Rev., X, 52 (1917).

neighborhood of the foil, the characteristics of the system are similar to those of a source of sound consisting of a diaphragm of small mass and stiffness actuated by a constant alternating force. The radiation resistance, which varies with the position of surrounding objects, may in this case be an appreciable part of the mechanical impedance of the system.

Equation of Thermal Equilibrium of an Ideal Gas.

The differential equation of heat conduction for a continuously varying temperature in a solid is well known. The corresponding equation for gases, which is made the basis of the following study of the action of the thermophone, is obtained by putting the rate of increase of heat content of an element of volume of the gas equal to the rate at which work is done upon it plus the heat received by conduction. We thus get

$$\rho c_v \frac{DT}{Dt} = -Ap\rho\frac{DV}{Dt} - K\nabla^2 T,$$

where $V = 1/\rho$ is the specific volume of the gas. Since for an ideal gas $p = \rho RT$ and $c_p - c_v = AR$, this equation reduces to

$$\rho c_p \frac{DT}{Dt} - A\frac{Dp}{Dt} - K\nabla^2 T = 0. \tag{1}$$

The loss by radiation is small in any practical case and so has been neglected.

Thermophone with Heating Element of Metal Foil.

Pressure Produced by a Periodic Change in Temperature of a Metal Strip Within a Small Enclosure.—If the temperature of the foil varies periodically, a temperature wave will be set up in the medium surrounding the foil. At acoustic frequencies these waves are attenuated to a small fraction of their original amplitude at distances small compared with the dimensions of the foil. Hence, in this discussion these thermal waves may be regarded as plane waves; also, since the fluid velocity is small, D/Dt is very nearly equal to $\partial/\partial t$. If then the temperature of the strip is given by $\Theta_0 + \Theta_1 e^{i\omega t}$, where Θ_1 is small compared with Θ_0, and if second order effects are neglected,

$$T = T_0 + T_1 e^{i\omega t},$$
$$p = p_0 + p_1 e^{i\omega t},$$
$$\rho = \rho_0 + \rho_1 e^{i\omega t},$$

and from (1) it follows that

$$\rho_0 c_p i\omega T_1 - Ai\omega p_1 - K\frac{\partial^2 T_1}{\partial x^2} = 0. \tag{2}$$

In the solution of this equation ρ_0 and K may be assigned the values that obtain at the temperature of the foil, since at points near the foil the gas has approximately the same temperature as the foil itself. If the dimensions of the enclosure are small compared with a wave-length of sound, p_1 is independent of x. The complete solution of (2) then is

$$T_1 = Ce^{\sqrt{2i}\alpha x} + De^{-\sqrt{2i}\alpha x} + \frac{k-1}{k}\frac{\Theta_0}{p_0}p_1,$$

in which α is set equal to $\sqrt{\frac{\rho_0\omega c_p}{2K}}$, and k is the ratio of the specific heats.

The boundary conditions require that for $x = \infty$, T_1 shall not be ∞ and for $x = 0$, T_1 shall equal Θ_1. Hence,

$$T_1 = \left(\Theta_1 - \frac{A\omega p_1}{2\alpha^2 K}\right)e^{-\sqrt{2i}\alpha x} + \frac{k-1}{k}\frac{\Theta_0}{p_0}p_1. \tag{3}$$

Also

$$p_1 = \frac{2p_0 a}{T_a V_0}\int_0^{V_0/2a} T_1 dx,^1 \tag{4}$$

where V_0 is the volume, and T_1 the mean temperature of the gas in the enclosure. Since, in all practical cases, $e^{-V_0\alpha/2a}$ is small compared with unity, it follows from (3) and (4) that

$$\Theta_1 = \frac{k-1}{k}\frac{\Theta_0}{p_0}\left[1 - \left(1 - \frac{k}{k-1}\frac{T_a}{\Theta_0}\right)\frac{V_0\alpha}{2a}(1+i)\right]p_1. \tag{5}$$

This equation gives the periodic pressure within the enclosure in terms of the periodic temperature variation of the heating element. The problem remains to express Θ_1 in terms of quantities that can be measured directly.

Temperature of the Heating Element.—Consider the case in which the thermophone element is heated by both direct and alternating currents, *i.e.*, by a current equal to $I_0 + I_1 \cos \omega t$ amperes. If I_0 is large compared with I_1, the rate at which heat is developed in the foil is approximately equal to the real part of

$$0.239RI_0^2 + 0.478RI_0I_1e^{i\omega t} \text{ calories per second.}$$

Equating this value to the rate with which heat is lost by radiation and conduction plus the rate with which it is stored in the foil, we get for the fundamental frequency

$$04.78RI_0I_1 = 8aC\Theta_0^3\Theta_1 - 2aK\left(\frac{\partial T}{\partial x}\right)_{x=0} + a\gamma i\omega\Theta$$

$$= \Theta_1(a\gamma i\omega + 2a\alpha K\sqrt{2i} + 8aC\Theta_0^3) - \frac{Aa\omega\sqrt{2i}}{\alpha}p_1, \tag{6}$$

[1] See Arnold and Crandall, Phys. Rev., N.S., Vol. X, 32 (1917).

where C is the radiation constant of the foil and γ is the heat capacity per unit area of foil. Reintroducing the time factor and retaining only the real part, we get finally from (5) and (6) for the pressure developed within the enclosure,

$$p_1' = \frac{0.478 R I_0 I_1 \cos(\omega t - \Phi)}{\left[\left(GQ - RF - \frac{A a \omega}{\alpha}\right)^2 + \left(FQ + RG - \frac{A a \omega}{\alpha}\right)^2\right]^{1/2}}, \tag{7}$$

where

$$F = \frac{V_0 \alpha T_a}{2 a p_0}\left(1 - \frac{k-1}{k}\frac{\Theta_0}{T_a}\right),$$

$$G = \frac{V_0 \alpha T_a}{2 a p_0}\left[1 - \frac{k-1}{k}\frac{\Theta_0}{T_a}\left(1 - \frac{2a}{\alpha V_0}\right)\right],$$

$$Q = 2 a \alpha K + 8 a C \Theta_0^3,$$

$$R = a \gamma \omega + 2 a \alpha K,$$

$$\Phi = \tan^{-1} \frac{FQ + GR - \frac{A a \omega}{\alpha}}{GQ - RF - \frac{A a \omega}{\alpha}}.$$

In these expressions α and K must be assigned values corresponding to the temperature of the foil. If K_0 and α_0 are the values at 0° C., then

$$K = K_0\left(\frac{\Theta_0}{273}\right)^{1/2}; \qquad \alpha = \alpha_0\left(\frac{273}{\Theta_0}\right)^{3/4}.$$

The Thermophone with Cylindrical Heating Element.

For laboratory purposes it is generally more practicable to use a thermophone with a heating element of metal foil instead of Wollaston wire as proposed by DeLange.[1] However, there are some cases in which the latter is of value as a standard source of sound, particularly in measurements on ear sensitivity. Thermophones of this type can readily be placed within the ear passage. Complications arising from stationary waves are thus almost entirely eliminated.

Pressure Within an Enclosure Containing a Cylindrical Wire of Variable Temperature.—Consider an airtight cylindrical enclosure along the axis of which is placed a wire of small diameter, having a temperature which can be represented by the expression $\Theta_0 + \Theta_1 e^{i\omega t}$. As before, the fluid velocity in the surrounding medium is small so that the relation (1) reduces to

$$K\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right) + A\frac{\partial p}{\partial t} - c_p \rho \frac{\partial T}{\partial t} = 0. \tag{8}$$

[1] Proc. Royal Soc., 91A, p. 239 (1915).

For the equation corresponding to (2) we have

$$\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} - 2i\alpha^2\right) T_1 = -\frac{i\omega A p_1}{K}. \tag{9}$$

If, as before, α is assumed to be constant, the complete solution of (9) is

$$T_1 = AJ_0(\sqrt{-2i}\alpha r) + BH_0(\sqrt{-2i}\alpha r) + \frac{k-1}{k}\frac{\Theta_0}{p_0}p_1.^1$$

The boundary conditions require that, as r approaches ∞, T_1 shall not approach ∞, and when r is equal to a, the radius of the wire, T_1 shall be equal to Θ_1. Hence

$$T_1 = \frac{\left(\Theta_1 - \frac{k-1}{k}\Theta_0\frac{p_1}{p_0}\right)}{H_0^{(2)}(\sqrt{-2i}\alpha a)} H_0^{(2)}(\sqrt{-2i}\alpha r) + \frac{k-1}{k}\Theta_0\frac{p_1}{p_0} \tag{10}$$

corresponding to (4) we have in this case the relation:

$$p_1 = \frac{p_0 l}{T_a V_0}\int_a^R T_1 2\pi r dr, \tag{11}$$

where R is the radius of the cylindrical enclosure, and l the length of the wire. In any practical type of thermal receiver R is large compared with a, and $aH_1^{(2)}(\sqrt{-2i}\alpha a)$ is large compared with $RH_1^{(2)}(\sqrt{-2i}\alpha R)$, so that to a close approximation we have from (10) and (11)

$$p_1 = \frac{2p_0\pi a l\left(\frac{k-1}{k}\frac{\Theta_0}{p_0}p_1 - \Theta_1\right)H_1^{(2)}(\sqrt{-2i}\alpha a)}{\sqrt{-2i}\alpha V_0\left(T_a - \frac{k-1}{k}\Theta_0\right)H_0^{(2)}(\sqrt{-2i}\alpha a}. \tag{12}$$

Temperature of the Heating Element.—Setting the rate with which heat is supplied to the wire equal to the rate with which heat is lost by conduction and radiation plus the rate with which heat is stored, we obtain the following relation

$$\begin{aligned} 0.478RI_0I_1 &= l\left[-2\pi aK\left(\frac{\partial T}{\partial r}\right)_{r=a} + 8\pi aC\Theta_0^3\Theta_1 + \gamma' i\omega\right] \\ &= l\left[\gamma' i\omega\Theta_1 + 2K\pi\frac{\sqrt{-2i}\alpha a H_1^{(2)}(\sqrt{-2i}\alpha a)}{H_0^{(2)}(\sqrt{-2i}\alpha a)}\left(\Theta_1 - \frac{\omega A p_1}{2\alpha^2 K}\right)\right. \\ &\qquad \left. + 8\pi aC\Theta_0^3\Theta_1\right], \end{aligned} \tag{13}$$

[1] The notation here used for the Bessel functions is the same as given in Jahnke and Emde, "Functionen-tafeln," p. 90 ff.

where γ' is the heat capacity per unit length of the wire. Let

$$\frac{H_0^{(2)}(\sqrt{-2i\alpha a})}{H_1^{(2)}(\sqrt{-2i\alpha a})} = M + iN.$$

We then get from (12) and (13)

$$0.478RI_0I_1 = \left[(\gamma' i\omega + 8\pi aC\Theta_0^3)\left(\frac{k-1}{k}\frac{\Theta_0}{p_0}l - \frac{(1-i)\left(T_a - \frac{k-1}{k}\Theta_0\right)V_0}{2p_0\pi a}(M+iN)\right) + \frac{2i\alpha^2KV_0\left(T_a - \frac{k-1}{k}\Theta_0\right)}{p_0}\right]p_1. \tag{14}$$

In general, $8\pi aC\Theta_0^3$ is small compared with $\gamma'\omega$. For example, in the case of a thermophone having a wire heating element, 0.0003 cm. in diameter, for a frequency of 25 cycles per second and $\Theta_0 = 800°$ absolute, the error, introduced by neglecting $8\pi aC\Theta_0^3$ in (14), even for these extreme conditions, is only 4 per cent. If then $8\pi aC\Theta_0^3$ is neglected, we obtain finally for the real part of p_1, the alternating pressure developed within the enclosure,

$$p_1' = \frac{0.956\pi ap_0}{\left(T_a - \frac{k-1}{k}\Theta_0\right)\alpha V_0\omega\gamma'}\frac{RI_0I_1\cos(\omega t - \Phi)}{\left[(N-M)^2 + \left(\frac{k}{k-1}\frac{2\pi aAp_0}{\alpha\Theta_0\gamma'} + \frac{2\pi al}{V_0\alpha\left(\frac{k}{k-1}\frac{T_a}{\Theta_0} - 1\right)} - (M+N)\right)^2\right]^{1/2}}, \tag{15}$$

where

$$\Phi = \tan^{-1}\frac{\left[\frac{k}{k-1}\cdot\frac{2\pi aAp_0}{\alpha\Theta_0\gamma'} + \frac{2\pi al}{V_0\alpha\left(\frac{k}{k-1}\frac{T_a}{\Theta_0} - 1\right)} - (M+N)\right]}{N-M}.$$

In the calculation of the values of $N - M$ and $M + N$ for small values of αa, it is convenient to use the following approximation formulæ,

$$N - M = 2\alpha a\left[\log_e\frac{\alpha a}{\sqrt{2}} + 0.577\right]; \qquad N + M = \frac{\alpha a}{2}.$$

These formulæ are correct to within a few per cent. for values of αa even as large as 0.15. For larger values of αa, M and N may be calculated from the tables given in Jahnke and Emde's "Functionentafeln" pp. 139–140. $H_\nu^{(2)}(\sqrt{-i}X)$ is the conjugate complex quantity of $H_\nu^{(1)}(\sqrt{i}X)$.

Values for the maximum pressure developed have been calculated by the above formulæ for thermophones having the following constants.

I. Heating element of metal foil: volume of the enclosure = 14 cu. cm., thickness of the gold foil = 0.79×10^{-5} cm., area of the gold foil = 5.5 sq. cm., $\Theta_0 = 335°$ absolute, $T_a = 300°$ absolute.

II. Heating element of Wollaston wire: volume of the enclosure = 1 cu. cm., diameter of the wire = 0.0003 cm., length of the wire = 1 cm., $T_a = 300°$ absolute, $\Theta_0 = 335°$ absolute.

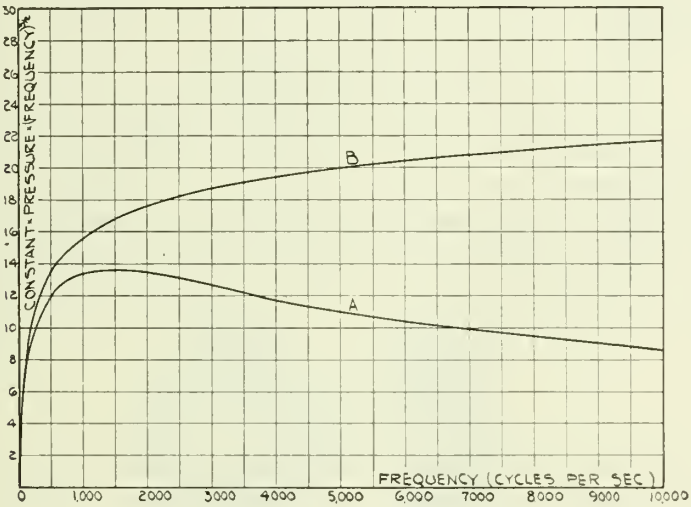


Fig. 1.

Frequency characteristics of thermophones.

A. Cylindrical heating element.

B. Flat-strip heating element.

In Fig. 1 the products of pressure and the 3/2 power of the frequency are plotted as a function of frequency. The curves thus show the amount of deviation from a simple 3/2 power relation. It appears that as telephone receivers the two types of instruments produce approximately the same amount of distortion and so neither possesses an advantage in this regard.

In the preceding analysis the heating element was assumed to lie along the axis of a cylindrical enclosure. But since the temperature

waves emanating from the wire have a large attenuation and a short wave length, the equations apply without alteration to any case in which the wire is located near the central part of the enclosure.

Further Considerations of the Formulæ.

In the preceding discussion the following assumptions have been made: The walls of the enclosure are non-conductors of heat, the temperature of the foil has the same value throughout its entire length, and at the surface of the foil the gas has the same temperature as the foil itself. Although for most practical cases these assumptions do not introduce inaccuracies of any consequence into the formulæ, the order of magnitude of the errors will here be considered.

If the walls are perfect conductors, as is approximately true in most cases, it may be shown that a first order correction is obtained by multiplying (7) by

$$\sqrt{1 - \frac{S}{V_0\alpha} + \frac{S^2}{2V_0^2\alpha^2}},$$

where S is the area of the walls of the enclosure. This factor is in general nearly unity.

In practice, the ends of the foil are held between comparatively massive clamps, so that almost no temperature variation at these points is produced by the alternating current. To take account of this fact the values of p_1' as given by equations (7) and (15) should be multiplied by

$$\sqrt{1 - \frac{2}{\alpha' l} + \frac{2}{(\alpha' l)^2}},$$

where l is the length of the element and α' is the value of α for the heating element. It may be shown that this factor gives the correction to the first order and is in general also nearly equal to unity.

When heat flows from a solid wall to a gas, the temperature corresponding to the velocity with which a molecule leaves the wall after a single impact will not be the same as the temperature of the wall. This fact is equivalent to a temperature drop between the solid and the gas.[1] This temperature drop at the surface of the foil is given by

$$\Delta\Theta = -\gamma\left(\frac{\partial T}{dx}\right)_{x=0},$$

where γ is a constant depending on the gas and its mean free path and on the condition of the surface of the solid wall. For hydrogen and a

[1] Kundt and Warburg, Pogg. Ann., 156, p. 177 (1875).

smooth solid surface on platinum it is equal to 7.25λ,[1] where λ is the mean free path of the molecules of the gas. For normal atmospheric conditions we find in this case to a first approximation $\Delta\Theta_1 = 3 \times 10^{-4} f^{1/2}\Theta_1$. For a frequency as high as 10,000 cycles this is only $0.027\Theta_1$ or less than 3 per cent. of the maximum value of the periodic temperature of the foil. For all practical purposes, therefore, the temperature drop at the surface of the foil may be disregarded.

Experimental Verification of the Theory of the Thermophone with Heating Element of Metal Foil.

(*a*) *Comparison of Thermophones having Different Physical Constants.*—There appears to be no way in which the pressure produced by a thermophone within an enclosure can be measured over its useful frequency range. The validity of equation (7), therefore, cannot be tested in a direct way. However, the alternating pressure exerted on the diaphragm of an electrostatic transmitter by thermophones having different physical constants may be compared. Whatever the sensitivity of an electrostatic transmitter as a function of frequency may be, it does not vary appreciably with time. Thus it is possible to determine at a number of fixed frequencies whether the alternating pressure varies with the different physical constants in accordance with equation (7). Experiments to this end have been carried out for a wide range of frequencies.

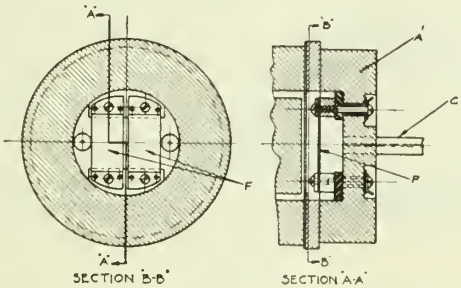


Fig. 2.

Thermophone in place for calibrating an electrostatic transmitter.

The thermophone was placed in front of the electrostatic transmitter in the manner shown in Fig. 2. The face of the transmitter together with the brass block, *A*, form an enclosure in which the heating elements, *F*, are centrally located. The enclosure is airtight except for the two equal capillary tubes, *C*. By means of these tubes gas is passed at a slow rate through the enclosure. To keep the pressure at atmospheric value, the pressure head on the intake tube is made equal to the suction

[1] S. Weber, A.d.P., 54, 439 (1917).

head on the outlet tube. These capillary tubes have a high impedance to the transmission of sound waves so that they do not affect the magnitude of the alternating pressure within the enclosure.

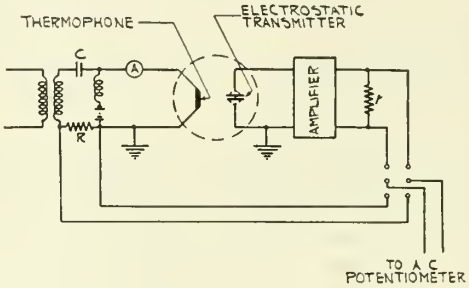


Fig. 3.

Circuit for calibrating an electrostatic transmitter with a thermophone.

The circuit used in the measurements is shown in Fig. 3. The ratio of the alternating potential drop across r and R was determined with an *a.c.* potentiometer.[1] This ratio multiplied by R and divided by the amplification of the amplifier gives the ratio of the voltage generated by the electrostatic transmitter to the alternating current passing through the thermophone heating element. The voltage per unit of pressure was then calculated by equation (7). Measurements were made with platinum foil, 6.81×10^{-5} cm. $\times$ 1.0 cm. $\times$ 5.35 cm., within an enclosure of 25.25 cu. cm. capacity, and with gold foil, 7.85×10^{-6} cm. $\times$ 1.0 cm. $\times$ 5.5 cm., within an enclosure of 13.9 cu. cm. capacity, both with hydrogen and with air within the enclosure. The conductivity of air was taken as 5.68×10^{-5} and of hydrogen, 41.6×10^{-3} c.g.s. units.

The values of voltage per dyne pressure as obtained with these thermophones for a particular electrostatic transmitter are given in the following table.

TABLE I.

Frequency	Gold Foil in Hydrogen.	Gold Foil in Air.	Platinum in Air.	Platinum in Hydrogen.
Cycles per sec.				
60	6.75		6.75	
300	4.85	5.00	4.82	
600	4.40	4.45	4.47	4.47
1000	4.20	4.30	4.45	4.30
2000	4.06	4.20		4.25
4000	4.40			4.55

[1] E. C. Wente, A Vacuum-Tube Alternating Current Potentiometer, Journal of the A.I.E.E., 40, p. 900, December, 1921.

It is seen from this table that the different thermophones yield practically the same results. Observations were not extended over the whole frequency range for each thermophone, since equation (7) applies only for a limited region. The frequency must be lower than the resonant frequency of the enclosure, and the wave length of the temperature wave emanating from the foil must be small compared with the dimension of the enclosure.

At the lower frequencies the predominating quantity in the denominator of equation (7) for gold in hydrogen is $2\alpha K$, while for platinum in air it is $\gamma\omega$. The tests, therefore, cover extreme conditions. Hence the fact that the values obtained with the different thermophones lie very near together is evidence for the correctness of equation (7), on the basis of which they were determined.

(*b*) *Comparison with a Pistonphone.*—If at some part of the frequency range it is possible to determine by an independent method the sensitivity of the electrostatic transmitter, a more direct experimental check of formula (7) can be obtained. Measurements were made on the electrostatic transmitter similar to those just described but with the thermophone replaced by a pistonphone. The construction of this apparatus is shown in Fig. 4. This pistonphone is similar to that described in a

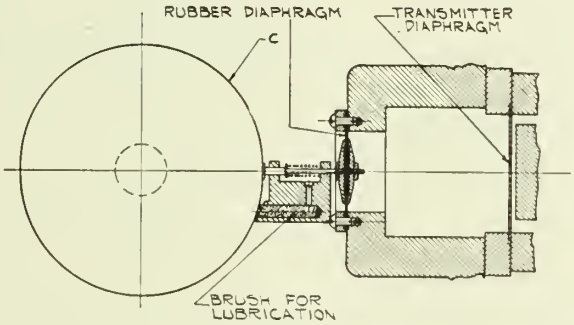


Fig. 4.

Use of pistonphone for calibrating an electrostatic transmitter.

former paper,[1] except that a cam, C, is used, which is cut so that with uniform rotation, a simple harmonic motion of 2 cycles per revolution is imparted to the piston. The pressure exerted on the diaphragm is given by

$$\frac{kp_0\sigma\xi \cos \omega t}{V_0}\sqrt{1 - \frac{S}{V_0\alpha} + \frac{S^2}{2V_0^2\alpha^2}}, \qquad 16)$$

[1] E. C. Wente, Phys. Rev., X, p. 48 (1917).

where σ is the effective area of the face of the piston,

S is the area of the walls of the enclosure,

$\xi \cos \omega t$ is the displacement of the piston.

The last factor in (16) takes account of the fact that, due to the heat conduction of the walls, the compression does not take place quite adiabatically.

A diagram of the circuit used in this test is shown in Fig. 5. If the electrostatic capacities of the transmitter and voltmeter are known, the open-circuit voltage of the transmitter may be determined from the voltmeter readings. Measurements were made for frequencies ranging from 10 to 200 cycles per second. The open-circuit voltages per dyne pressure are plotted in Fig. 6 together with values obtained for the same electrostatic transmitter with a gold leaf-hydrogen thermophone. The points are seen to lie very near together. This fact shows that for this frequency range the absolute value of the pressure produced by the thermophone as a function of frequency is correctly given by equation (7). At the lower frequencies the pressure produced by the thermophone varies with the different factors entering into the

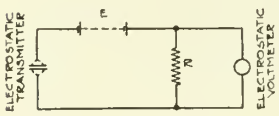


Fig. 5.

Circuit for calibrating electrostatic transmitter with pistonphone.

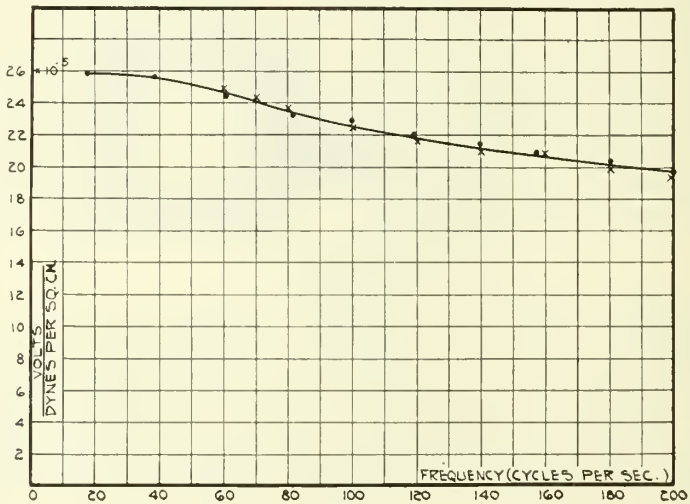


Fig. 6.

Efficiency of electrostatic transmitter.

• Values obtained with the pistonphone.

× Values obtained with the thermophone.

expression (7) more than at the higher frequencies. Therefore, it is reasonable to assume that this expression also gives correct values at higher frequencies.

The Use of the Thermophone for Measurements of the Thermal Conductivity of Gases.

One cause of uncertainty in the measurements with the thermophone is the fact that the thermal conductivity of gases is not well known. For example, in the case of hydrogen good authority can be found for values which differ from each other as much as 15 per cent. The thermophone suggests itself as a possible method for determining the conductivity of a gas. The principal source of error in conductivity measurements as heretofore carried out lies in the transport of heat by convection currents. In the case of the thermophone this source of inaccuracy is entirely eliminated.

Various arrangements of the apparatus for carrying out thermal conductivity measurements with the thermophone could be suggested. Some independent method of measuring an alternating pressure or producing one of known magnitude is required. Apparatus of the pistonphone type is perhaps the simplest arrangement that could be devised for the purpose.

Research Laboratories of the
American Telephone and Telegraph Co.
and the Western Electric Co., Inc.,
November 1, 1921.

ATOMIC RADII. I.[1]

By Maurice L. Huggins.[2]

Synopsis.

The Physical Meaning of Bragg's "Atomic Spheres" and "Atomic Radii."—W. L. Bragg's "atomic spheres" and "atomic radii," considered in the light of the Lewis theory of atomic and molecular structure, have a definite physical meaning. *The "atomic sphere" of an atom is its valence shell, and its "atomic radius" is the distance from atomic center to a group of electrons (usually an electronpair) in the valence shell.* This idea is applied to several crystals.

Bragg's Method of Calculating Atomic Radii not always Valid.—Bragg's assumption that the distance between two adjacent atomic centers equals the sum of their radii is often not valid, since in many cases the group of electrons constituting the bond does not lie on the line joining the atomic centers; in other words, the two atomic "spheres" overlap.

Factors Affecting the Atomic Radius.—The various factors affecting the distance from atomic nucleus to valence group—the atomic radius—are discussed, with examples.

COMPARISONS of molecular and atomic volumes, computed from measurements of the densities of crystals, have often been made. The volume allotted to each atom of a given element, however, is found to vary greatly in different crystals, and, aside from giving a rough idea of the periodic variation of the size of the atom with atomic number, such comparisons have not been of very great value.

The Meaning of "Atomic Radius."—Of much wider application is the idea of "atomic radii," concerning which W. L. Bragg has written[3] in the Philosophical Magazine. He assumes each atom to be a sphere, or at least to possess a certain "sphere of influence," the size of which is practically constant for a given element in all crystals; also that each atom is held in position by touching the atoms around it. On these assumptions the distance between the centers of two adjacent atoms is equal to the sum of their atomic radii.

In diamond, for instance, in which each carbon atom is equidistant from four others,[4] each atomic sphere just touches those around it, the points of tangency being oriented with respect to the center of the atom

[1] This article is an amplification of a paper presented before the Berkeley meeting of the American Physical Society, Aug. 4, 1921, the abstract of which appears in the Phys. Rev. (2), *18*, 333 (1921).

[2] Dupont Fellow in Chemistry, Univ. of California, 1921–22.

[3] Phil. Mag. (6), *40*, 169 (1920).

[4] Bragg and Bragg, X-Rays and Crystal Structure, G. Bell & Sons, 1918, p. 102.

as are the four corners of a regular tetrahedron with respect to its center. The radius of the carbon atom is then exactly half the distance between atomic centers.

One of the ideas at the foundation of modern organic chemistry is that of the tetrahedral orientation of the four bonds by which a carbon atom is usually connected to other atoms. These bonds have been identified by G. N. Lewis[1] with pairs of electrons. It is but a step further to assume that each of the points of tangency of Bragg's hypothetical atomic spheres represents a pair of electrons, whenever the number of electrons required for such an arrangement is equal to the number of valence electrons present in the crystal. This requirement is met in diamond, for each carbon atom, being tetravalent, supplies four valence electrons to the structure—one to each of the valence pairs around it.

Application to Crystals.[2]—In a crystal of sphalerite, ZnS,[3] each zinc atom is surrounded by four equidistant sulfur atoms, and each sulfur atom by four equidistant zinc atoms. Each sulfur atom, according to the Lewis theory of valence and atomic structure,[4] has six valence electrons, and we may assume that zinc, being divalent, has two. This gives an average of four per atom, as in diamond, and we may again assume electronpairs on the centerlines between adjacent atoms—at the points where atomic spheres touch. Here also there is a tetrahedron of pairs around each sulfur and each zinc atom, as would be expected from the Lewis theory and the author's extension of it to the heavier elements.[5]

In iron pyrites (FeS_2), according to Bragg,[6] each iron sphere touches six sulfur spheres and each sulfur sphere is tangent to three iron spheres and one sulfur sphere. If we assume, as before, that the points of tangency represent electronpairs, then there is an octahedron of pairs around each iron atom and a tetrahedron of pairs around each sulfur. There are fourteen electrons per FeS_2 group required for this arrangement, which is what we should expect from atomic theory, each iron supplying two valence electrons and each sulfur six.

In each of the foregoing crystals the electronpairs are on (or very near, in the case of FeS_2) the centerlines between atoms, and the distance between closest atoms equals the sum of their atomic radii. In many crystals this is not the case—the valence electrons are not on the center-

[1] J. Am. Chem. Soc., *38*, 762 (1916).

[2] The electronic structures of diamond, ZnS, FeS_2, $CaCO_3$, and many other crystals are given and discussed by the author in an article soon to be published in the J. Am. Chem. Soc.

[3] Bragg and Bragg, loc. cit., p. 97.

[4] Loc. cit.

[5] J. Am. Chem. Soc., "Electronic Structures of Atoms," soon to be published.

[6] Bragg and Bragg, loc. cit., p. 127; W. L. Bragg, loc. cit.

lines, the atomic spheres overlap, and atomic radii can not be computed by Bragg's method.

As examples may be mentioned crystals of the alkali halides and of many of the metals. Let us consider a crystal of sodium fluoride, NaF, for instance. According to the Lewis theory a neutral sodium atom possesses one and a neutral fluorine atom seven valence electrons. In a crystal of NaF, each sodium valence electron has passed into the valence shell of a fluorine atom, producing the charged Na^+ and F^- ions. The structure of these ions may be represented [1] as $[(+11)(2\times1)(4\times2)]^+$ and $[(+9)(2\times1)(4\times2)]^-$ respectively. Each ion consists of a nucleus of charge $(+11)$ or $(+9)$ surrounded by an inner shell of two electrons, (2×1), and an outer shell of four electronpairs, (4×2), arranged at the corners of a tetrahedron, of which the nucleus is the center.

It has been shown[2] that the Na^+ and F^- ions are disposed at alternate corners of a simple cubic lattice, each sodium being symmetrically surrounded by six fluorines and each fluorine by six sodiums. Now it is impossible for these ions to be placed in the crystal in such a way that there will be a pair of electrons on each of the centerlines between adjacent ions. The symmetry requirements are such that the electronpairs must be on the *diagonals* of the small cubes of the lattice, somewhat as represented in Fig. 1. In this figure, for simplicity, only the electron-

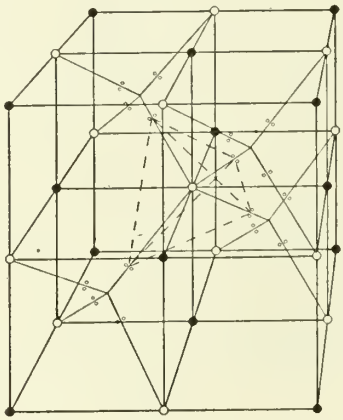


Fig. 1.

Arrangement of atomic centers and of sodium *or* fluorine electronpairs in NaF.

pairs in *one* kind of ion (Na^+ *or* F^-) are shown; those in the other are similarly placed, probably in the alternate cubes (left vacant in the diagram) of the structure.

[1] Huggins, "Electronic Structures of Atoms," loc. cit.

[2] Hull, Proc. Am. Inst. Elec. Eng., *38*, 1189 (1919). Davey, PHYS. REV. [2], *18*, 102 (1921).

The outer electronpairs of the ions in crystals of the other alkali halides are placed in a similar manner on the diagonals of the small cubes of the lattice. It is evident that in such structures as these, we are not justified in using Bragg's simple method of calculating atomic radii.

As a matter of fact, the atomic radius of sodium in a sodium fluoride crystal has very little meaning, unless we define it more explicitly. The sodium's only valence electron has gone into the valence shell of a fluorine atom. Should we consider the radius of sodium as the distance from a sodium nucleus to one of the fluorine valence pairs; should we take it equal to the radius of the sodium kernel; or should we assume it to be the distance between nearest atomic centers less the radius of the fluorine atom, calculated from other crystals, as does Bragg? In crystals of many of the metals a similar question arises. Perhaps it will be best not to use the term "atomic radius" at all in discussing such a crystal as this.[1]

[1] Since the above was written, an abstract of a paper by W. P. Davey has appeared, Phys. Rev. (2), *18*, 102 (1921), in which "radii" of alkali and halide *ions* are calculated on the assumptions (1) that the distance between atomic centers equals the sum of the radii, and (2) that the radii of K^+, Rb^+ and Cs^+ are equal respectively to those of Cl^-, Br^- and I^-.

The first assumption has just been shown to be invalid, but it is easy to see that, if the distance from nucleus to the outermost shell of an ion of a given element in different crystals is practically constant, the interatomic distances, *although not equalling the sum of the ionic radii*, will be approximately additive. (The actual values calculated have very little significance.)

The second assumption is probably nearly correct, for, the atomic radius of a *complete* atomic shell decreases but slowly as the nuclear charge is increased (considering the elements at the end of a period of the periodic system, *e.g.*, C, N, O, F, Ne, Na). However, the checks obtained by Davey from the interatomic distances of different crystals do not necessarily substantiate this assumption any more than they do the first, for if the "radius" of each negative ion were a certain distance *greater* than that assumed, and that of each positive ion were the same distance *less* than that assumed, the distance between centers of positive and negative ions would in each case be the same as that already computed.

It may similarly be said of Bragg's atomic radii calculations, that if his value for the radius of sulfur should prove to be too high, then practically all of the radii calculated directly or indirectly from this value for electronegative elements are too high and those calculated for electropositive elements are too low.

In this connection it is interesting to note a paper by R. N. Pease (J. Am. Chem. Soc., *43*, 991 (1921) and Chem. News, *123*, 121 (1921)) largely "devoted to establishing the fundamental correctness of the assumption that the outer shells of electrons in isosteres [atoms or groups of atoms having the same number and arrangements of electrons outside of the nuclei, but differing in the nuclear charges] have the same dimensions independent of the charges on the positive nuclei of the atoms or at least that the volume of the molecule as a whole shall behave as if this were the case" The approximate equivalence of the molecular volumes calculated for isosteres is merely the result of the fact that, except for hydrogen, the only atoms in the compounds compared are those of electronegative elements and the rare gases,—those near the ends of the periods of the periodic system, the very elements in which, as we have just stated, the atomic radius varies but slightly (but surely varies) with the atomic number (or nuclear charge).

In calcite, $CaCO_3$, each calcium atom is surrounded by six equidistant, symmetrically arranged oxygen atoms, each carbon atom by three equidistant oxygen atoms at the corners of an equilateral triangle and each oxygen atom by two similarly placed calcium atoms and one carbon atom. Each calcium supplies to the structure two valence electrons, each carbon four, and each oxygen six, a total of 24 for each $CaCO_3$ unit. Assuming the pair as the unit, as in diamond and sphalerite, there can be but one pair to each of the six identical calcium-oxygen bonds. There remain then 12 electrons to be distributed between three exactly equivalent carbon-oxygen bonds. There are four ways to do this in accord with the symmetry of the structure. Each carbon might be surrounded by six pairs *in one plane*, as in Figs. 2*A* and 2*B*; or each

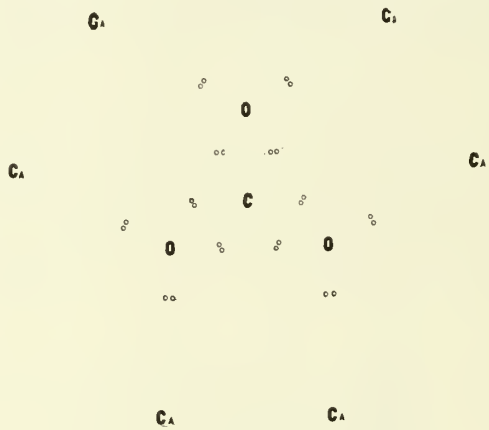


Fig. 2*A*.

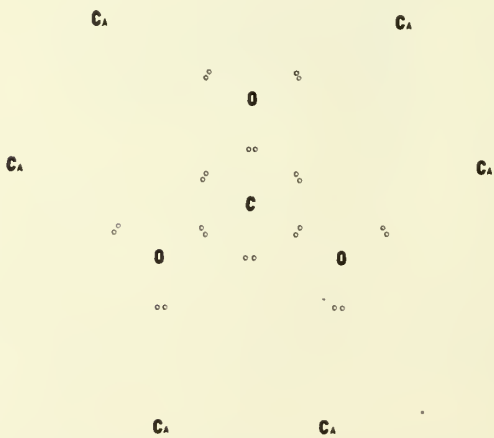


Fig. 2*B*.

carbon might be surrounded by but three pairs and each oxygen by four pairs, these last being *all in the same plane.*

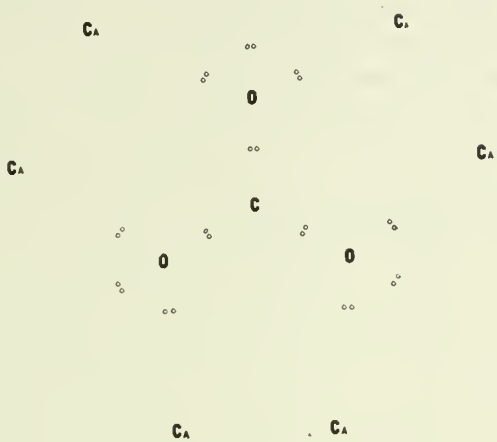


Fig. 2*C*.

Possible (but improbable) electron arrangements in calcite.[1]

By far the most probable arrangement, and the only one in which the arrangement of electrons around each oxygen atom is what we know it to be in other crystals, is that shown in Fig. 3. Each carbon is con-

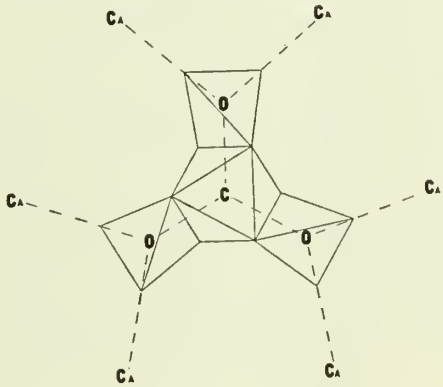


Fig. 3.

nected to the surrounding oxygens by double bonds. An octahedron of pairs is thus formed around each calcium and each carbon atom, and a tetrahedron of pairs around each oxygen atom.

If we assume this to be the correct structure, it is evident that the atomic spheres of the carbon and oxygen atoms interpenetrate, and their

[1] The calcium atoms in Figs. 2 and 3 are not in the plane of the paper, but are alternately above and below it.

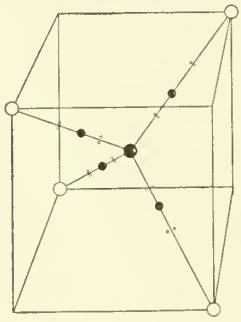
radii, therefore, do not add up to give the distance between atomic centers.[1]

Causes of Variation of the Atomic Radius of an Element.—Let us now consider briefly the chief factors affecting the distance between atomic center and valence electronpair—the atomic radius—for a given element.

In the first place, in many crystals some of the valence pairs do not act as bonds. These are surely at a different distance from the nucleus—probably a smaller distance—than pairs which are bonds. In a crystal of quartz (SiO_2),[2] for example, each oxygen atom has a valence shell of four electronpairs, only two of which serve as bonds.

Second, for one reason or another, a valence electronpair may be forced away from its normal position in the valence shell.[3] This we might expect to result in an increased distance between nucleus and valence pair. Thus in the quartz crystal the angle subtended at the atomic center by the two bond electronpairs around each oxygen atom is considerably greater than it would be (about 109°) if the pairs were in their normal positions at the corners of a regular tetrahedron. Another good example of this is found in the marcasite (FeS_2) crystal. The distortions of the atoms in this substance have been discussed quite fully by the writer elsewhere.[4]

Third, widely varying pulls are exerted on electronpairs by atoms of different elements, hence the atomic radius depends to a considerable extent on the kind of atom to which the atom in question is bonded. We should not expect the radius of the oxygen atom to be exactly the same in the compounds ZnO, FeO, Cu_2O, and SiO_2. In the ammonium chloride crystal[5] (Fig. 4) the distance of each hydrogen nucleus from the valence pair connecting it to the nitrogen atom is surely different from that bonding it to the chlorine atom, hence, using the term in the sense in which it has been employed in this paper, the radius of the hydrogen atom in this crystal has two different values.[6]



●N •H ○Cl

Fig. 4.

[1] This calcite structure practically proves that the double bond is what it has long been thought to be; at the same time it disproves the old idea that the carbon atom is *always* tetrahedral in shape.

[2] Huggins, PHYS. REV. (2), xix., p. 363 (1922).

[3] The author has shown that, in general, except for elements in the first row of the periodic table, valence pairs *tend* to place themselves opposite the centers of the faces of the next underlying atomic shell of electrongroups (*i.e.*, on lines passing through the center of the atom and the center of each face of the outermost kernel shell).

[4] PHYS. REV. (2), xix., p. 369 (1922).

Fourth, an atom of the same element in different structures may pull an electronpair away a different distance from the nucleus of the atom to which it is bonded. An example of this is found in the two forms of zinc sulfide—sphalerite and wurzite—which differ only in the way the layers of atoms are placed over one another. The distance between planes of zinc and sulfur atoms is found to be slightly greater in wurzite than in sphalerite.

Fifth, if an atom has a different number of electronpairs in its valence shell in two crystals, we should not expect their distances from the nucleus to be the same in the two cases. Thus, each carbon atom is surrounded by four pairs in diamond and by six in calcite.

Sixth, valence electronpairs are pulled out from the nucleus to a different extent according to whether they are on the centerlines or not. This may have some effect on the oxygen radius in quartz, for it is probable that the electronpairs bonding each oxygen to silicon atoms are not on the Si—O centerlines. Whenever this is the case, the radius computed by Bragg's method will not be the true radius.

Seventh, many atoms are capable of more than one arrangement of electrons in that part of the atom inside of the valence shell, which Lewis has designated the "kernel." This manifests itself in a variability of the number of valence electrons and of the atomic radius. An extreme example of this is probably furnished by the element manganese (for which Bragg gives two values of atomic radius, 1.17 Å. and 1.47 Å.).

Eighth, in some crystals, notably in graphite[1] the electronic structure of which is to be described in a forthcoming paper, and in many organic compounds, the number of electrons constituting a bond is more than two. Wherever this is the case, the distances from the atomic nuclei to these electrongroups (and also to electronpairs in the same crystal) are quite different from the atomic radii of the same atoms in other crystals. In diamond the atomic radius of carbon is 0.77 Å.; in graphite each atomic center is surrounded by three electronsextets and one electronpair, the distance to each being about 1.45 Å.

Berkeley, Calif.

[5] Bragg and Bragg, loc. cit., p. 158; Bartlett and Langmuir, J. Am. Chem. Soc., *43*, 84 (1921); Huggins, "Electronic Structures of Crystals II," soon to be published.

[6] In this case we might properly speak of the "diameter" of the hydrogen atom, meaning the distance through the atomic nucleus from electronpair to electronpair; but in considering atoms in which there are not two valence pairs on diametrically opposite sides of the nucleus (which is the case for most atoms in most crystals), the term "atomic diameter" has no physical meaning.

THE CRYSTAL STRUCTURES OF ARAGONITE ($CaCO_3$) AND RELATED MINERALS.

By Maurice L. Huggins.[1]

Synopsis.

The Structure of Aragonite.—A structure is proposed for aragonite which is in accord with all observed facts. As in calcite, each carbon atom is bonded (by double bonds) to three oxygen atoms, each oxygen to two calciums and one carbon, and each calcium to six oxygens, at the corners of an irregular octahedron. The distortions of the structure are considerable; their magnitudes and causes are discussed.

Cleavage Planes.—The observed cleavage of aragonite is shown to be in accord with the following principles:—(1) Cleavage tends to occur so as to leave the two new crystal surfaces electrically neutral. (2) Where some bonds are weaker than others, cleavage will take place in such a way as to rupture the weaker bonds in preference to the stronger ones. (3) All bonds being equally strong, cleavage will occur between the planes connected by the fewest bonds per unit area.

The Structures of $SrCO_3$, $BaCO_3$ and $PbCO_3$.—The dimensions and interatomic distances in the isomorphous minerals strontianite, witherite and cerussite, which are assumed to have similar structures, are computed.

Electron Arrangements in Accord with the Author's Theory.—These structures are shown to be in conformity with the author's theory that the electrongroups in an atomic shell tend to place themselves opposite the faces of the imaginary polyhedron formed by the electrongroups in the next underlying shell.

ALTHOUGH the structure of calcite has been known for several years,[2] the arrangement of the atoms in aragonite, the orthorhombic form of $CaCO_3$, has not heretofore been published.

The arrangement of the electrons in calcite has been obtained, with the aid of the Lewis theory of atomic and molecular structure,[3] by the author.[4] We might expect the electronic and atomic arrangement about each atom to be very similar in the two crystals. By provisionally assuming this, the author has been able to work out the aragonite structure.

The Arrangement of Carbon and Calcium Centers.—The arrangement of the centers of carbon and calcium atoms is illustrated in Figs. 1, 2 and 3. Carbon atoms are represented by dots, calcium atoms by circles. The lines in Figs. 1 and 3 indicate which C and Ca atoms are bonded together

[1] Dupont Fellow in Chemistry, University of California, 1921–22.

[2] W. L. Bragg, Proc. Roy. Soc., *A89*, 468 (1914). Bragg and Bragg, X-rays and Crystal Structure, G. Bell and Sons, 1919, p. 112. Wyckoff, Am. Jl. Sci. (4), *50*, 317 (1920).

[3] G. N. Lewis, J. Am. Chem. Soc., *38*, 762 (1916).

[4] Huggins, Phys. Rev. (2) xix, p. 346, 1922.

(through oxygen atoms) although they do not show the actual positions of the bonds. Fig. 1 shows the arrangement in each 001 (basal) plane. These planes are laid over one another in such a way as to produce a face-centered lattice, the unit of which is shown in Fig. 2. Fig. 3 gives

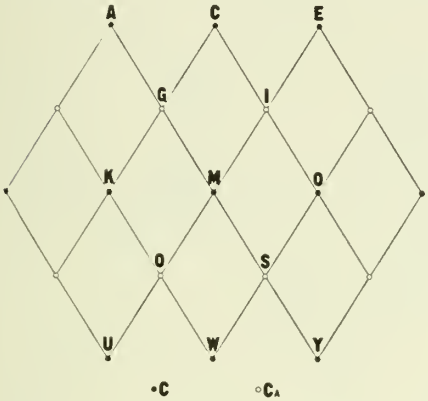


Fig. 1.
Arrangement of C and Ca atoms in each 001 plane.

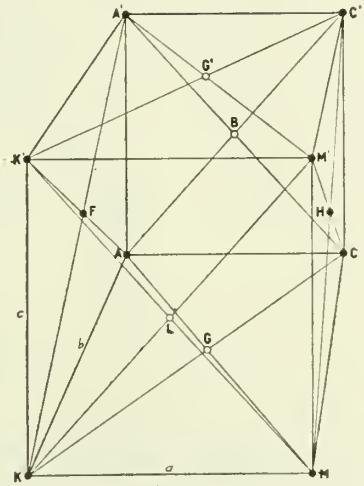


Fig. 2.
Unit cell. C and Ca atoms only.

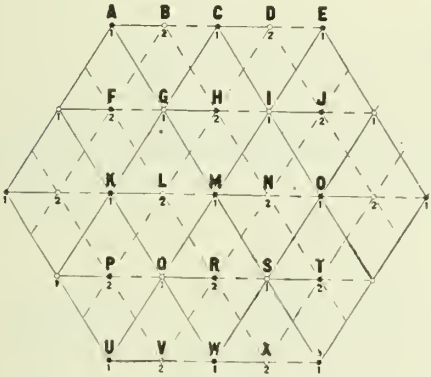


Fig. 3.
Plan C and Ca atoms only.

the structure in plan. The atoms are numbered to indicate in which plane each atomic center lies. Lines between atoms in planes 1 and 1 or 1 and 2 are shown full; those between atoms in planes 2 and 2 or 2 and 1′ (the next plane above 2) are dotted. The lettering in each of these diagrams corresponds to that in the others.

The Arrangement of Oxygen Atoms and Valence Electrons.—Fig. 4 shows the arrangement of calcium and oxygen atoms around each carbon atom in calcite. The central octahedron, H, is a carbon atom, the sur-

rounding tetrahedra are oxygen atoms, and the letters D, B, G, L, N, and I′ show the relative positions of the calcium atoms. Each oxygen is surrounded by four pairs of electrons, at the tetrahedron corners, two

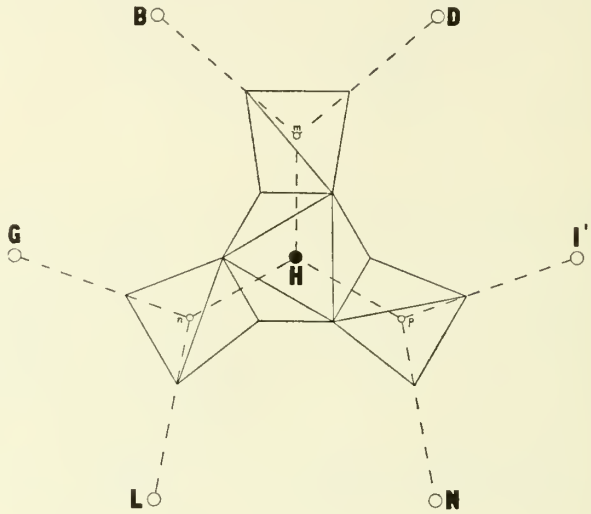


Fig. 4.

Arrangement around a carbon atom (H), in both calcite and aragonite.

of which serve as bonds connecting it to the adjacent calcium atoms, and two forming a double bond joining it to the carbon atom (H). This gives six pairs of electrons, at octahedron corners, around each carbon atom. Each calcium atom is also surrounded by six electronpairs at octahedron corners.

This same arrangement exists in aragonite, although it is distorted to some extent. The carbon atom H, for instance, is bonded, through oxygen atoms, to calcium atoms D, B, G, L, N, and I′, as shown in Fig. 5. (In this figure and in Fig. 6 the lines represent bonds between atoms.) The positions of the oxygen atoms and of the valence electronpairs, relative to the other atoms, is thus approximately determined, for we may assume the distance from carbon center to oxygen center to be practically the same as in calcite (1.28 Å.[1] = 1.28×10^{-8} cm.).

The Dimensions of the Lattice, and Distances between Atoms.—We shall now calculate the actual dimensions of the structure. Groth [2] gives the density of aragonite as 2.926 — 2.933 g./c.c. and the axial ratio as $a : b : c = 0.6228 : 1 : 0.7204$ (= KM : KA : KK′, Fig. 2).

[1] W. L. Bragg, Nature *106*, 725 (1921).

[2] Chemische Krystallographie, Vol. II., p. 206.

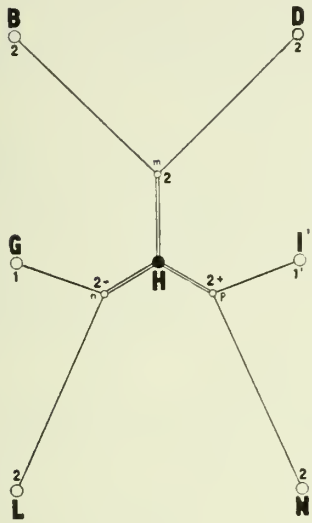


Fig. 5.

Arrangement around a carbon atom (H).

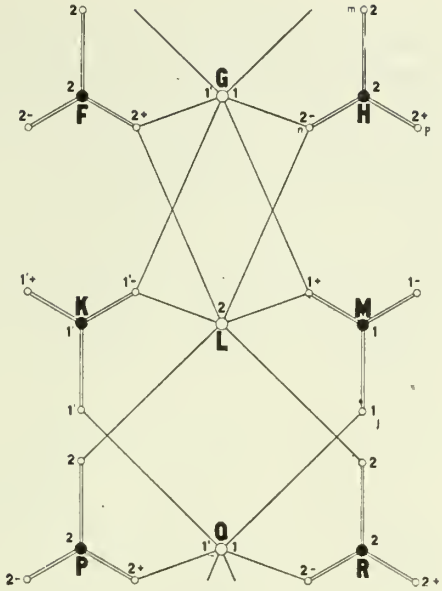


Fig. 6.

Arrangement around a calcium atom (L).

The volume of the unit cell is equal to

$$\frac{\text{no. molecules per cell} \times \text{molec. wt.}}{\text{no. molecules per mol} \times \text{density}} = \frac{2 \times 100.075}{0.6062 \times 10^{24} \times 2.9295} \text{ cm.}^3$$

$$= 112.7 \times 10^{-24} \text{ cm.}^3$$

Then

$$b = \text{KA} = \sqrt[3]{\frac{112.7 \times 10^{-24} \text{ cm.}^3}{0.6228 \times 0.7204}} = 6.310 \times 10^{-8} \text{ cm.} = 6.310 \text{ Å.}$$

From this

$$a = \text{KM} = 0.6228 \times 6.310 \text{ Å.} = 3.930 \text{ Å.}$$

and

$$c = \text{KK}' = 0.7204 \times 6.310 \text{ Å.} = 4.546 \text{ Å.}$$

The calcium-carbon distance in calcite (HB = HD = HI, etc., Fig 4) is given by W. L. Bragg[1] as 3.206 Å. The corresponding distances in aragonite, calculated from the unit distances given above, are

$$\text{HB} = \text{HD} = \text{HN} = \text{HL} = 3.717 \text{ Å}, \qquad \text{HI}' = \text{HG} = 3.004 \text{ Å}.$$

The calcium-carbon-calcium angle in calcite ($\angle$BHD = $\angle$I'HN, Fig. 4) is 78° 05′. In aragonite $\angle$BHD = 63° 50′ and $\angle$I'HN = 69° 46′.

[1] Nature *106*, 725 (1921).

It is evident from the above comparison, that although the general arrangement of atoms is the same and the distances in the two crystals between corresponding atoms are approximately the same, there is considerable distortion (chiefly in the *b* direction) of the structure in aragonite from the more symmetrical marshalling of calcite. This may largely be accounted for in the following way:

Let us assume, for this purpose, that the distance between nearest calcium and carbon centers (HI′, HD, HN, etc.) *tends* to be 3.206 Å. and that the Ca—C—Ca angle (∠BHD, ∠I′HN, etc.) tends to become 78° 05′. Now if *a* and *c* had the values calculated for them, and if ∠I′HN were 78° 05′, the distance HN and the angle LHN (= ∠BHD) would have to be 6.22 Å. and 36° 48′, respectively. On the other hand, if *a* and *c* were as calculated, and HN were 3.206 Å., then angles LHN and I′HN would be 75° 34′ and 66° 23′, respectively.

It is apparent that with the kind of structure assumed it would be impossible for the Ca—C distances HI′ and HN to both be the same as in calcite, if ∠I′HN were 78° 05′ (as in calcite); and vice versa. The actual structure is a compromise between these two extremes (for which calculations were made in the preceding paragraph). ∠I′HN is 69° 46′, intermediate between 66° 23′ and 78° 05′, and HN is 3.717 Å., intermediate between 3.206 Å. and 6.22 Å. ∠LHN, 63° 50′, is also midway between the extremes 36° 48′ and 75° 34′.

HI′ in aragonite (Fig. 5) is slightly less than the corresponding distance HI′ in calcite (Fig. 4). This may be attributed to the tendency of a valence electronpair to be drawn closer to the nucleus (of oxygen, in this case) if another pair (or other pairs) in the same valence shell is pulled out away from the nucleus by any cause.[1]

We have here an excellent example of the variability of the distance between the nucleus and a valence electronpair (the atomic radius) for a given element. If the distance from nucleus to one electronpair is about 24 per cent. greater than that to another *in the valence shell of the same atom*, then we must be very careful about assuming these distances (the atomic radii) to be the same for a given element in different crystals, which have entirely different structures. The variation in radius is, in general, very much less for electro-negative elements than for electro-positive elements, the alkali and alkaline earth elements showing the greatest variation.[2]

Cleavage Planes.—Cleavage planes in a crystal, the author assumes to be determined, in general, by the following considerations:

[1] Cf. Lewis, loc. cit.; Latimer and Rodebush, J. Am. Chem. Soc., *42*, 1419 (1920); and Huggins, idem., "Electronic Structures of Some Organic Compounds," soon to be published.

[2] Huggins, PHYS. REV. (2) xix, p. 346, 1922.

1. Cleavage tends to occur so as to leave the two new crystal surfaces electrically neutral.

2. Where some of the bonds in a crystal are weaker than others,[1] cleavage will take place in such a way as to rupture the weaker bonds in preference to the stronger ones.

3. All bonds being equally strong, cleavage will occur between the planes connected by the fewest bonds per unit area (of the cleavage plane).

Without considering here the justification for the above assumptions, it will be pointed out that they are in full accord with the aragonite structure which has been described, and the observed cleavage planes of aragonite crystals.

According to Groth[2] the most marked cleavage is between the 010 planes, imperfect cleavage occurring parallel to the 110 and 011 planes, but none between 001 or 100 planes.

Now we may be sure, from chemical considerations, because oxygen and carbon atoms hold onto electrons more tightly than do calcium atoms, that whenever a rupture occurs, it will be between a calcium kernel and the valence pair by which it is bonded to an oxygen kernel. This will leave an excess positive charge on the calcium and an excess negative charge on the oxygen, or, perhaps we should say, on the carbonate group. So, according to the first condition given above, cleavage must be in such a way as to leave an equal number of these positive calcium atoms, and also of the negative carbonate groups, on each side of the break, it being impossible for the cleavage plane to separate a plane containing only calcium atoms from one containing only carbonate groups. This at once eliminates the 100 and 001 planes, as may be seen from Fig. 3.

Since the distances (HB, HD, HN, etc., Fig. 5) between calcium and carbon atoms in the same 001 plane are much greater than those (HG, HI′) between carbon and calcium atoms in different 001 planes, we may feel sure that the Ca—O distances Bm, Dm, Ln, Np, etc., are greater than the distances Gn, I′p, etc. It seems reasonable to assume, then, that the former Ca—O bonds are weaker than the latter. In accordance with this and with condition 2 above, is the marked cleavage between 010 planes, this being the only way in which it may occur without causing the rupture of any of the bonds of the Gn, I′p type. Cleavage in the 110 and 011 directions ruptures fewer bonds (either considering all the Ca—O

[1] By the strength of a bond is here meant the force resisting breakage in the direction normal to the cleavage plane being considered. Hence a bond normal to the cleavage plane must be considered to have a greater "strength"—for this purpose—than a similar bond not normal to the plane of cleavage.

[2] Loc. cit.

bonds or only those of the stronger type) per unit area than that in any other direction (except those already considered). Here also the observed result is in accord with the principles outlined above.

Comparison with $BaCO_3$, $SrCO_3$ and $PbCO_3$.—Isomorphous with aragonite are the minerals strontianite ($SrCO_3$), witherite ($BaCO_3$) and cerussite ($PbCO_3$).[1] From the densities, axial ratios and molecular weights, the dimensions of the unit cell have been computed for each of these, exactly as was done for aragonite; also the angle BHD and the distances (Fig. 5) BH, HN and Bm (the metal-oxygen distance, calculated on the assumption that Hm, the carbon-oxygen distance, is 1.30 Å. in each crystal).[1] These are given in Table I., alongside of the aragonite values.

TABLE I.[2]

	Aragonite $CaCO_3$.	Strontianite $SrCO_3$.	Witherite $BaCO_3$.	Cerussite $PbCO_3$.
Density (g./c.c.)....	2.926–2.933	3.680–3.716	4.28–4.37	6.574
Vol. of unit cell = 2 × molec. volume.	112.7 Å.[3]	131.7 Å.[3]	150.6 Å.[3]	134.1 Å.[3]
Axial ratio $a : b : c$.	0.6228 : 1 : 0.7204	0.6090 : 1 : 0.7237	0.5949 : 1 : 0.7413	0.6102 : 1 : 0.7232
a (KM).....	3.930 Å.	4.072 Å.	4.158 Å.	4.102 Å.
b (KA).....	6.310 Å.	6.686 Å.	6.989 Å.	6.723 Å.
c (KK′).....	4.546 Å.	4.838 Å.	5.181 Å.	4.862 Å.
HB.....	3.717 Å.	3.914 Å.	4.066 Å.	3.938 Å.
HI′.....	3.004 Å.	3.162 Å.	3.322 Å.	3.181 Å.
Bm.....	2.70 Å.	2.88 Å.	3.02 Å.	2.91 Å.
∠BHD.....	63° 50′	62° 40′	61° 30′	62° 47′

Atomic Theory.—In a previous paper the writer has presented a system of atomic structures (practically identical with the Lewis theory for the lighter elements), which is based largely on the idea that the electrongroups (pairs or triplets) in an atomic shell tend to occupy positions opposite the centers of the faces of the imaginary polyhedron formed by the electrongroups in the next underlying shell.[4] Thus, if the underlying shell consists of eight electrongroups arranged at cube corners, the next shell further out will consist of six groups, at the corners of an

[1] Bromlite, $(Ba, Ca)(CO_3)_2$, and manganocalcite, RCO_3, in which R represents Mn, Mg, Ca, and a little Fe, might also be included, but their compositions, and hence their densities and axial ratios, are variable.

[2] The densities and axial ratios are obtained from Groth, loc. cit.; in each case the mean of the values given for the density was used in the computations.

[3] The average of the values 1.28 Å. and 1.30 Å. given for this distance in calcite and rhodochrosite ($MnCO_3$), respectively, by W. L. Bragg, Nature *106*, 725 (1921).

[4] The arrangements of electrons in atoms of elements in the first row of the periodic table are governed by other considerations.

imaginary octahedron, each of which is opposite a face of the underlying cube. This idea is of great importance in the determination and discussion of crystal structures, for the number of valence electrons and the relative positions which they tend to occupy are the chief factors which determine the arrangement of the atoms in a crystal of a given substance.

It has been shown in other papers that, in a great many cases at least,[2] the arrangement of valence pairs in crystals is in accordance with the foregoing idea, each pair being oppositeaface of the next kernel shell underneath, in both atoms connected by the pair (if it is acting as a bond, and so is in two valence shells).

The crystals discussed in this paper are no exceptions to this rule. The outermost kernel shell, in a calcium, strontium, or barium atom, consists of a cube of pairs, and the structure we have assigned to these crystals indicates that there are six pairs around each metal atom, arranged at the corners of a somewhat distorted octahedron—that is, opposite the faces (but not the *centers* of the faces) of the kernel cube. Some of the causes of the distortions have already been discussed. The outermost shell in the kernel of a *divalent* lead atom, if the author's structure for it is correct, consists of six pairs at the corners of an octahedron. Now an octahedron has eight faces, but in the lead carbonate crystal only six of them are occupied by valence pairs (the two unoccupied faces being on diagonally opposite sides of the atom). These six are themselves at the corners of a distorted octahedron. As a matter of fact, since the angle between cube diagonals is 70° 32′, whereas that between diagonals of a regular octahedron is 90°, and the actual angle between bonds in these crystals is in the neighborhood of 62° or 63°, the displacement of the bonds from what we might call their normal positions—through the centers of the faces of the kernel polyhedra—is much less for lead than for calcium, strontium or barium. This is as we should expect, for lead is much less electropositive than the alkaline earths, and we have every reason to believe that its valence electrons are more closely

[1] Huggins, Phys. Rev. (2), xviii, p. 333, 1921, and Phys. Rev. (2), xix, p. 346, 1922.

[2] The orienting effect of the kernel upon the valence electrons is much less in the alkali and alkaline earth elements, where the valence electrons are not drawn close to the kernel, than in more electronegrative elements.

Most of the alkali halides, the alkaline earth oxides and sulfides, a few other binary compounds, and many of the metals possess a somewhat different type of structure, in which the atoms are held together by what may be called "distributed bonds," in which the valence pairs are not on the centerlines between nearest atoms, rather than "localized bonds" of the ordinary single or double bond type. In these crystals also, however, there is a manifest tendency for electronpairs *or groups of electronpairs* to be placed opposite the faces of the underlying atomic shells.

and more tightly held than those of the other metals under consideration. (The metal-oxygen distance Bm is practically the same for lead as for strontium, although the atomic numbers are 82 and 38, respectively.)

It is of interest in this connection that in crystals of smithsonite ($ZnCO_3$), magnesite ($MgCO_3$) and some other minerals isomorphous with calcite, the valence shell of the metal atom consists of six electronpairs, at octahedron corners, outside of a kernel shell of four pairs, at tetrahedron corners.[1] The state of affairs is here just the opposite of that in lead carbonate. Only half of the eight faces of the *valence* shell are occupied (*on the inside*) by *kernel* pairs. This arrangement is symmetrical, however, and seems to be possible where the valence pairs are drawn far enough away from the kernel by the attractions of other atoms.[2]

BERKELEY, CALIF.

[1] Many cases of a tetrahedron outside of an octahedron are known. Cf. the author's paper last referred to.

[2] Other examples of this phenomenon, existing outside of the crystalline state, are afforded by the compounds H_2SiF_6 and SF_6, in each of which there is a valence shell of six pairs outside of a kernel shell of four pairs.

THE CRYSTAL STRUCTURE OF QUARTZ.

By Maurice L. Huggins.[1]

Synopsis.

The Structure of Quartz (SiO_2).—By means of the Lewis theory, a structure has been obtained for quartz which accounts in a satisfactory way for the crystalline form, crystal symmetry, optical rotation, hardness, high melting point, insolubility, and x-ray spectra of the substance. It is in strict accord with the conclusions of W. H. Bragg in regard to the structure. Furthermore, the distance between adjacent silicon and oxygen atoms, calculated from the dimensions of the lattice, as obtained by Bragg, is approximately equal to the sum of their atomic radii, obtained from other crystals.

The Arrangement of Atoms and Electrons.—Each silicon atom is surrounded by four pairs of electrons at tetrahedron corners, which act as bonds connecting it to four equidistant oxygen atoms. Each oxygen atom is also surrounded by four tetrahedrally oriented electronpairs, two of which serve as bonds connecting the oxygen to silicon atoms. *The crystal is thus not made up of SiO_2 units, but is a single molecule*, for all of the bonds around each silicon or each oxygen atom are of the same type—the usual type of bond which connects the atoms in a molecule.

QUARTZ crystals are placed by crystallographers in the trapezohedral class of the trigonal system, possessing three-fold symmetry about a vertical axis, but having neither plane of symmetry nor center of symmetry. They are enantiomorphic, being of two kinds, which are to each other as an object and its mirror image, and which rotate polarized light in opposite directions. The usual form of crystal is that of a hexagonal prism, terminated at each end by a pyramid, some of the corners, however, being modified by small faces of other types.

W. H. Bragg[2] has obtained x-ray reflections from several faces of a quartz crystal, his measurements being, in the main, such as would be

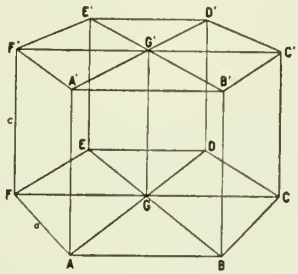


Fig. 1.

[1] Dupont Fellow in Chemistry, University of California, 1921–22.

[2] W. H. Bragg, Proc. Roy. Soc., *A89*, 575 (1914); Bragg and Bragg, X-Rays and Crystal Structure, G. Bell and Sons, London, 1918, page 160.

obtained if the scattering centers were at the points of a triangular prism lattice (Fig. 1) of dimensions, $a = 4.89$ Å. (1 Ångstrom unit $= 10^{-8}$ cm.) and $c = 5.375$ Å. However, the reflections from the basal planes were such as to indicate a distance between planes just one-third of c, or 1.792 Å. Also it was calculated, from the density of the crystal, that three molecules of SiO_2 are associated with each point of the lattice. Bragg therefore reasoned that the structure is based on three interpenetrating lattices of the type shown, these being "so related that they can be derived from each other by a rotation of $2\pi/3$ about, and a translation $c/3$ along, an axis parallel to the c direction. Thus each trigonal axis of the structure has points arranged spirally around it, and since a spiral may be either right- or left-handed, we can understand the reason for the two forms of quartz."

This was as far as Bragg could go. He was not able to determine either the amount of the relative displacement of the interpenetrating lattices or the disposition of the atoms around the points of these lattices. It has been found possible, however, by means of the Lewis theory of valence and atomic structure,[1] which the author has successfully applied [2] to the structure of a large number of crystals, to obtain a complete solution of the structure, which is in entire accord with Bragg's conclusions.

According to the Lewis theory, there are sixteen valence electrons per SiO_2 group—six per oxygen atom and four per silicon atom. Each oxygen and each silicon atom tends to surround itself by four pairs of electrons, arranged at the corners of a tetrahedron. These pairs may act as bonds, in which case they each form a part of the valence shells of two atoms, or they may be "lone pairs"—pairs not acting as bonds between atoms. It seems highly probable, moreover, from a consideration of analogous substances, that in the quartz crystal the bonds are all Si—O bonds.

If the above assumptions are correct—sixteen electrons per SiO_2 unit, a tetrahedron of pairs around each atom, and Si—O bonds only—then each silicon must be bonded to four oxygen atoms, arranged at the corners of a tetrahedron, and each oxygen atom must be bonded to two silicon atoms, which are also at two of the corners of a tetrahedron. (We should not expect this tetrahedron to be regular, for two of the electron pairs around each oxygen atom are lone pairs and two are bond pairs. The magnitude of this distortion and the effect on the structure will be discussed later in this paper.)

The Quartz Structure.—With the aid of the foregoing ideas the author has obtained the structure for quartz represented in plan in Fig. 2. In

[1] Lewis, J. Am. Chem. Soc., *38*, 762 (1916).

[2] Huggins, idem.

this figure there are shown three consecutive layers of atoms, each of which is normal to the trigonal axis. The atoms are numbered 1, 2 or 3, according to whether they are in the first, second or third layer from the bottom. The fourth layer is identical with the first, the fifth with the second, etc.; (3) means the layer, identical with 3, next below layer 1. The solid dots represent the centers of silicon atoms and the circles the centers of oxygen atoms. The double circle indicates that there are two oxygen atoms, in different layers, one over the other.[1] The bonds connecting the atoms are represented by full lines. These are of two lengths (in the diagram); the longer lines connecting atoms in the same layer; the shorter lines connecting atoms in different layers. (The actual distances between atomic centers are of course the same, or very nearly the same, in the two cases.) Each of these shorter lines is doubled, to represent, not a "double bond," but two single bonds, connecting a silicon in layer 2, for instance, with oxygens in layers 1 and 3, or a silicon in layer 1 with oxygens in layers (3) (below) and 2 (above).

Each silicon kernel is surrounded by four pairs of valence electrons, bonding it to four equidistant, tetrahedrally oriented, oxygen atoms, and each oxygen kernel by four tetrahedrally arranged electron pairs, two of which serve as bonds connecting the oxygen to two silicon atoms, the other two being lone pairs.

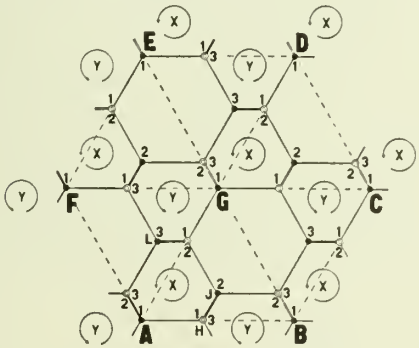


Fig. 2.

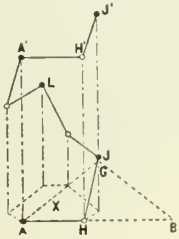


Fig. 3.

X and Y denote axes around each of which there is a spiral of silicon and oxygen atoms. One of these spirals is shown in Fig. 3. It may be readily seen from Fig. 2 that equivalent, similarly situated points in the structure (such as points X, or points A, B, C, D, E, F and G, the lettering in Figs. 1 and 2 corresponding) are at the points of a lattice of the type shown in Fig. 1. For each point of the lattice there are three silicon

[1] This is not strictly true because of their distortions. See the later discussion on this subject.

and six oxygen atoms, arranged spirally in three similar layers, the vertical distance between layers being just one third the height of the unit prism. Thus the x-ray spectra, the crystalline form, the existence of right- and left-handed crystals, and the optical rotation of the substance are all accounted for.

Distortions from the Structure Described.—Let us now consider the distortion from the structure shown in Figs. 2 and 3. Of the four electron pairs surrounding each oxygen kernel only two are acting as bonds, hence their arrangement cannot be that of a *regular* tetrahedron. It seems reasonable to suppose that the bond pairs are further from the atomic center than the lone pairs, and that the angle formed by the imaginary lines connecting the atomic center with the bond pairs is somewhat greater than 109° 28′, its value if the electron pairs were at the corners of a regular tetrahedron.

Since we do not know this angle, it is impossible either to compare this structure quantitatively with the known dimensions of the lattice, as determined by Bragg, or to calculate directly the exact position of the atoms relative to each other. But by assuming this structure to be correct, and taking the distance between adjacent silicon and oxygen atomic centers as equal to the sum of their atomic radii, obtained from other crystals, the angle between silicon-oxygen bonds can be calculated from the lattice dimensions. If it proves to be some value somewhat greater than 109° and considerably less than 180°, then this constitutes a rough check on the structure. Or, we may do what amounts to the same thing—we may calculate the Si—O distance on the assumption that the angle between bonds is 109° 28′; and this distance, if our reasoning is correct, should be a few per cent. greater than the distance calculated from the atomic radii. We shall see that this is the case.

If the angle between the two bonds connecting each oxygen to silicon atoms ($\angle AHJ$, Fig. 4) were 109° 28′, the distance between adjacent silicon and oxygen atom centers ($AH = HJ$), computed from the dimensions of the lattice, would be 1.97 Å. Now the radius of the silicon atom—the distance from atomic center to valence electron-pair—in a crystal of the element[1] is 1.17 Å. Bragg[2] computes the radius of the oxygen atom, from dimensions of the ZnSp, ZnS, and FeS_2 structures, to be 0.65 Å. Transferring these values of atomic radii to the quartz crystal, we get 1.82 Å. as the approximate distance between silicon and oxygen atomic centers.[3]

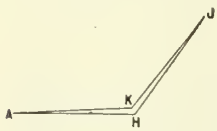


Fig. 4.

[1] Debye and Scherrer, Phys. Zeit., *17*, 277 (1916); Hull, PHYS. REV., (2) ix, 566, 1917; Gerlach, Physik. Zeitsch., xxii 557. 1921.

[2] Phil. Mag., *40*, 169 (1920).

Each oxygen atom in the crystal is then displaced from the position *H* (Fig. 4) to a position *K*, about 1.82 Å. from the nearest silicon atoms. If we make the assumption that *K* is in the same plane as *A*, *H* and *J*, then the angle *AKJ* between the oxygen-silicon bonds can be calculated to be about 125°.

We are now in a position to calculate the relative positions of the silicon atoms (*e.g.*, of *J*, Figs. 2 and 3, relative to *AB*). The calculations are but a matter of geometry and simple trigonometry, but the results based on the Si—O distance 1.82 Å. and the angle *AKJ* = 125°, are of interest (although they must only be considered approximate). The projection of the silicon atom *J* on plane 1 is on the perpendicular bisector of the line *AB*, at a distance of 0.73 Å. from *AB*. Similarly, the projection of *L* is on the perpendicular bisector of *AG*, and 0.73 Å. from it, etc.

Discussion.—This structure agrees with the Lewis theory in every particular—in the number of valence electrons, in their tetrahedral arrangement around the silicon and oxygen atoms, and in the fact that each bond is in reality a pair of electrons in the shells of two atoms at the same time. It should be noted further that the Si—O bonds are single rather than double bonds[1] (as would be expected from the formula O = Si = O), this being in accordance with a generalization made by Lewis, and accounted for on theoretical grounds by the author,[2] that the elements which form double bonds readily (*e.g.*, carbon, nitrogen, oxygen) are all in the first row of the periodic table. The silicon and oxygen atoms do not occur in SiO_2 units, it being impossible to tell with what oxygen atoms a given silicon atom was "originally" bonded (before crystallization). Every atom in the crystal is connected to every other atom through bonds which are all of the usual type connecting atoms in a molecule; hence the whole crystal is a single molecule.

We might represent an isolated SiO_2 molecule in this way

$$\begin{array}{ccccc} & \cdot\cdot & & \cdot\cdot & \\ : & O & : & Si & : & O & : \\ & \cdot\cdot & & \cdot\cdot & \end{array}$$

the electronpairs around both the oxygen and silicon atoms being understood to be at tetrahedron corners. Now the tendency of the silicon

[1] A double bond being a bond in which *two* pairs of electrons hold together two atoms.

[2] J. Am. Chem. Soc., "Electronic Structures of Atoms," soon to be published.

[3] This must be considered only an approximation, for the distance from atomic center to bond electronpair is surely different in a crystal in which all four valence pairs are acting as bonds (ZnO) from that in a crystal in which only two of them are bonds (SiO_2). Also, the bond pairs in quartz may not be quite on the centerlines between atoms, but slight displacements such as might be expected would have a negligible effect on the interatomic distances. Considering everything, the value 1.82 Å. is probably too small.

atom to surround itself by *four* electronpairs is very great, and it does this by attracting the oxygen atoms from two more molecules, giving the structure

```
        ..
      : O :
        ..
        Si
        ..
      : O :
   ..   ..   ..
 : O : Si : O :
   ..   ..   ..
      : O :
        ..
        Si
        ..
      : O :
        ..
```

The new silicon atoms attract more oxygens, and this process is continued indefinitely, the tetrahedral arrangement of the bonds producing the structure of quartz.

Crystal formation in this case, then, as in the case of most minerals, consists chiefly of a reaction between an atom (O) containing a lone electronpair in its valence shell and another atom (Si) capable of holding on to that lone pair, the result being a stable single bond. The stability of these bonds, in the case of quartz, is evidenced by its hardness, high melting point, insolubility, etc., which would be difficult to account for if the crystal were composed of saturated molecules held together by secondary valence.

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THE CRYSTAL STRUCTURES OF MARCASITE (FeS_2), ARSENOPYRITE (FeAsS) AND LOELLINGITE ($FeAs_2$).

By Maurice L. Huggins.[1]

Synopsis.

The Structure of Marcasite.—An arrangement of atoms and valence electrons, which is consistent with all known experimental facts, is proposed for marcasite (FeS_2). The arrangement around each atom is very similar to that in pyrite. The sulfur atoms are in pairs. Each sulfur is bonded, by pairs of electrons, to one sulfur and four iron atoms, and each iron atom to six sulfur atoms. Taking the unit distance from the dimensions of the pyrite structure, the density is computed, the value obtained being the same as that experimentally observed, within the limits of experimental error. The distortions of the atoms in the structure are discussed.

The Structures of Arsenopyrite (FeAsS) and Loellingite ($FeAs_2$).—Assuming the same general arrangement for arsenopyrite and loellingite as for marcasite, the dimensions of the unit cells are obtained, and these compared with those of marcasite.

Pyrite.—FeS_2 crystallizes in two forms, one (pyrite) being cubic, the other (marcasite) orthorhombic. By means of x-rays W. L. Bragg[2] has determined the structure of pyrite. He finds (Fig. 1*A*) that the

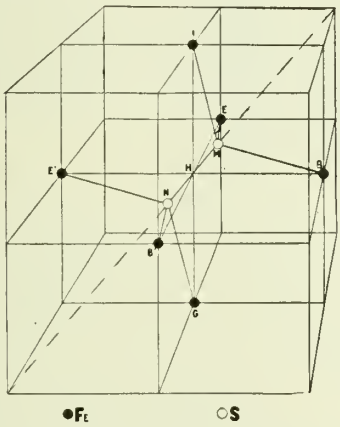

Fig. 1 *A*.

Illustrating the arrangement around each S–S group in pyrite.

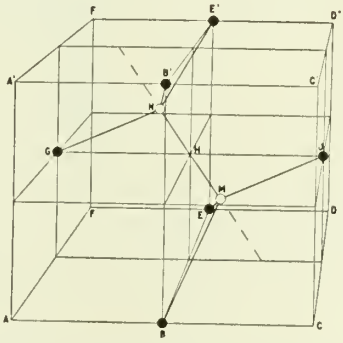

Fig. 1 *B*.

Illustrating the arrangement around each S–S group in marcasite.

sulfur atoms occur in pairs, each sulfur being surrounded by one sulfur and three iron atoms, at the corners of an imaginary tetrahedron. Each

[1] Dupont Fellow in Chemistry, Univ. of California, 1921–22.

[2] W. L. Bragg, Proc. Roy. Soc., *A89*, 468 (1913); Bragg and Bragg, X-rays and Crystal Structure, G. Bell & Sons, 1918, p. 127.

iron atom is surrounded by six sulfur atoms, at octahedron corners. As the author has previously pointed out,[1] if each iron furnishes two valence electrons to the structure, and each sulfur six, then there are fourteen electrons per FeS_2, just the number required for a pair of electrons on (or near) the centerlines between two adjacent atoms—each pair being in the valence shells of two atoms at the same time. This is in strict accord with the Lewis theory of the structure of atoms and molecules[2] and the author's extension of that theory.[3]

Marcasite.—Assuming that the arrangement of electrons and atoms around each iron or sulfur atom is substantially the same in marcasite as in pyrite, the writer has worked out a structure for the former substance which is in complete conformity with the known facts.

The arrangement of iron atoms around each S–S group is shown in Fig. 1 *B*. By comparing corresponding points (denoted by the same letters in the two diagrams) in Figs. 1 *A* and 1 *B*, it may be readily seen that the relative positions of atomic centers are practically the same in the two crystals. In Fig. 2 all the atoms and bonds in the unit parallel-

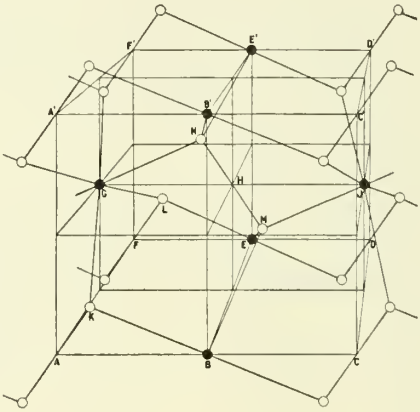

Fig. 2.

Marcasite.

opiped are represented. (The lettering corresponds to that in Figs. 1 *A* and 1 *B*.) The structure may be described as being composed of two interpenetrating lattices, one of which contains an iron atom at the corners and the center of the unit cell, and the other a pair of sulfur atoms at the corners and the center of the unit cell. Each of these

[1] J. Am. Chem. Soc., "Electronic Structures of Crystals. I," soon to be published.

[2] G. N. Lewis, idem, *38*, 762 (1916).

[3] Huggins, idem., "Electronic Structures of Atoms," soon to be published.

lattices is in turn made up of two interpenetrating lattices in which the iron atoms or the pairs of sulfur atoms are at the corners *only* of the unit cell, the difference between the two iron lattices or the two sulfur lattices being in the orientation of the atoms at the points of the lattices. The symmetry of the structure is such as to produce crystals belonging to the bipyramidal class of the orthorhombic system. Each iron atom is bonded to six sulfur atoms and each sulfur to three iron and one other sulfur atom.

The axial ratio of the marcasite crystal[1] has been given as $a : b : c = 0.7646 : 1 : 1.2176$. Preliminary calculations indicate that the distances AB, AF and AA' (Fig. 2) are in this proportion. Since the unit distance in the a direction is AC, rather than AB, the correct axial ratio is $a : b : c = AC : AF : AA' = 1.5292 : 1 : 1.2176$.

Bragg[2] has determined the distance GH (Fig. 1 A) in pyrite as 2.69 Å. (1 Ångstrom = 10^{-8} cm.). If now we assume the corresponding distance ($GH = AB$, Figs. 1 B and 2) in marcasite to be the same, then twice this, or 5.38 Å., is a, and the volume of the unit parallelopiped $ACDFA'C'D'F'$ is

$$5.38 \text{ Å.} \times \frac{5.38 \text{ Å.}}{1.5292} \times \frac{1.2176 \times 5.38 \text{ Å.}}{1.5292} = 81.08 \text{ Å.}^3$$

Since there are four sulfur atoms and two iron atoms in this parallelopiped, half of this, or 40.54 Å., is the volume per molecule. Multiplying by Avogadro's number gives the molal volume, and dividing the molecular weight by the molal volume gives the density, in grams per c.c.,

$$D = \frac{119.96}{0.6062 \times 10^{24} \times 40.54 \times 10^{-24}} = 4.882.$$

This is in good agreement with the observed density, which Groth gives as 4.85–4.88 g./c.c.

Distortions of the Atoms.—The distance BH ($= AG$) may be calculated, from the axial ratio and the value $AB = 2.69$ Å., to be 2.77 Å., which is somewhat greater than the corresponding distance AB. This may be accounted for as follows:

$\angle KGL$ must equal $\angle BME$. Now G is an iron atom bonded to six sulfur atoms, the bonds tending to form central angles of 90° with each other, while M is a sulfur atom bonded to four other atoms, the bonds tending to make a somewhat greater angle with each other (109° 28′ if the bonds were all identical). In pyrite the corresponding angle (*e.g.*, $\angle BME$, Fig. 1 A) between two S–Fe bonds is about 117°. We might

[1] Allen, Crenshaw, Johnston, and Larsen, Zeit. f. anorg. Chem., *76*, 201 (1912).

[2] Loc. cit.

then expect the angles KGL and BME to be between 90° and 117°, and such is the case. We may approximate their value by assuming the distance HM and the angle MHJ to be the same as the corresponding distance and angle in pyrite. $\angle BME$ may then be computed to be 102° 10′. From this, BM is 2.26 Å. and $\angle HMB$ is 108° 05′.

This last angle is several degrees greater than the Fe–S–S angle (Fig. 1, $\angle HMB$ = 102°) in pyrite, and it is largely for this reason that HB is greater than AB. Also, because the tetrahedra of electronpairs around the sulfur atoms and the octahedra of pairs around the iron atoms are considerably distorted, the distances between atomic centers are probably slightly greater than if the arrangement were perfectly regular.

Arsenopyrite and Loellingite.—It is interesting to compare the dimensions of arsenopyrite (FeAsS) and loellingite ($FeAs_2$) with those of marcasite. These, as well as a number of other minerals,[1] are in the same crystallographic class as marcasite and in all probability they possess similar structures, arsenic atoms replacing half or all of the sulfur atoms.[2]

Assuming that this is the case, it is possible to compute from the densities and axial ratios of the crystals the dimensions of the unit cells. These are given in Table I. The data are taken from Groth's Chemische

TABLE I.

	FeS_2.	FeAsS.	$FeAs_2$.
Density (g./c.c.).....	(4.88)	6.12–6.18	7.40
Molec. volume.....	40.5 Å.^{3}	43.6 Å.^{3}	45.8 Å.^{3}
$a : b : c$.....	1.5292 : 1 : 1.2176	1.3546 : 1 : 1.1882	1.3378 : 1 : 1.2831
$\frac{a}{2} = AB$.....	2.69 Å.	2.57 Å.	2.55 Å.
$b = AF$.....	3.52 Å.	3.79 Å.	3.82 Å.
$c = AA'$.....	4.28 Å.	4.51 Å.	4.71 Å.
$AG = BH$.....	2.77 Å.	2.945 Å.	3.025 Å.

Krystallographie, Vol. 1. For FeAsS the average value of the density is used. Groth's a is taken as $a/2$ in each case. The distance $AG = BH$ is also given, for comparison with AB.

It will be noted that the unit distance in the a direction actually decreases when arsenic replaces sulfur in the crystal, although without doubt the "radius" of the arsenic atom in crystals is greater than that

[1] Cf. Wherry, J. Wash. Acad. Sci., *10*, 487 (1920).

[2] The Braggs have shown that cobaltite, CoAsS, has the same type of structure as has pyrite. (X-rays and Crystal Structure, p. 154.)

of the sulfur atom.[1] On the other hand the replacement of sulfur by arsenic causes a considerable increase in the dimensions of the structure in the *b* and *c* directions. This can be interpreted as meaning that the As–S and As–As axes (*NM*) are more nearly normal to the basal planes than are the S–S axes. In other words, $\angle MHJ$ is greatest in $FeAs_2$ and least in FeS_2.

It is probable also that the atomic radius of iron—the distance from atomic center to valence pair—is slightly different in these compounds due to the fact that the charge on the atomic kernel is different in the three cases. In FeS_2 each iron atom furnishes two electrons to the valence bonds around it, in FeAsS three, and in $FeAs_2$ four, assuming each sulfur atom to furnish six and each arsenic five; for, as has already been stated, fourteen electrons per "molecule" are needed.

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[1] W. L. Bragg, Phil. Mag. (6), *40*, 169 (1920), gives 1.02 Å. for sulfur and 1.26 Å. for arsenic.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE ANNUAL MEETING, TORONTO, DECEMBER 28–30, 1921.

THE twenty-third annual meeting (the 112th regular meeting) of the American Physical Society was held in Toronto on December 28, 29 and 30, 1921, in affiliation with Section B—Physics—of the American Association for the Advancement of Science. Meetings were held in the lecture room of the Physical Laboratory at the University of Toronto. The attendance was about one hundred and fifty at the ordinary sessions; on Thursday, December 29, there was a joint session with Sections B and C, and the American Mathematical Society, the attendance then being about two hundred. On the evening of Friday, December 30, there was a dinner of the affiliated societies attended by about one hundred members and friends. The arrangements made by the local committee for the entertainment of the members were most excellent and the meeting was generally considered one of the most enjoyable that the Society has ever held.

The president of the Society, Theodore Lyman, presided at all sessions of the Society.

On the afternoon of Wednesday, December 28, 1921, the president of the American Physical Society, Professor Theodore Lyman, gave the official address on "The Spectroscopy of the Extreme Ultraviolet."

On the morning of Thursday, December 29, 1921, there was a joint session with the American Mathematical Society and Sections B and C of the American Association for the Advancement of Science. The presiding officers were G. W. Stewart, chairman of Section B, and W. D. Harkins, chairman of Section C. At this session Professor J. C. McLennan, the retiring vice-president and chairman of Section B, gave an address on "Atomic Nuclei and Extra-Nuclear Electronic Configuration." This address was followed by a Symposium on the Quantum Theory with the following speakers:

For Section C of the A. A. A. S., R. C. Tolman, The Fixed Nitrogen Research Laboratory, Washington.

For the American Mathematical Society, H. B. Phillips, Massachusetts Institute of Technology.

For the American Physical Society, Saul Dushman, General Electric Company.

The regular annual business meeting of the American Physical Society was held on Friday morning, December 30, 1921, at 11 o'clock. A canvass of the

ballots for Officers resulted in the election of the following officers for the year 1922:

For President: Theodore Lyman.

For Vice-President: C. E. Mendenhall.

For Secretary: D. C. Miller.

For Treasurer: G. B. Pegram.

For Members of the Council, four-year Term: H. G. Gale and D. L. Webster.

For Members of the Board of Editors of THE PHYSICAL REVIEW, *three-year term:* A. J. Dempster, E. P. Adams and A. L. Hughes.

At the meeting of the Council held on December 30, 1921, twenty-nine persons were elected to membership, seven were elected to fellowship and four were transferred: *Elected to Fellowship:* Kelvin Burns, Paul T. Epstein, Griffith C. Evans, Kyotoku Fuji, Victor Hess, Joel H. Hildebrand, and F. H. Norton; *Transferred to Fellowship:* Edward Bennett, Arthur J. Dempster, A. H. Patterson, Joseph Valasek; *Elected to Membership:* Hugh M. Ackley, L. M. Alexander, Ernest F. Barker, Perry Byerly, Jr., Herbert Kimball Cummings, John C. Deagan, Joseph W. Ellis, K. C. Fang, Chas. M. Heck, T. R. Hogness, Robert J. Hopkins, Douglas E. Howes, M. L. Huggins, Laurence M. Klauber, Hubert Mann, Charles R. Moore, Wayne B. Nottingham, Marcus D. O'Day, John Patterson, Clarence C. Schmidt, Paul John Searles, Russell E. Seidle, Hugo F. Sloctemyer, Raymond R. Starke, Wilson Taylor, Harold M. Terrill, Andrew Thomson, Yu Tai Yao, and Mr. Zanstra.

The Secretary reported the deaths of nine members and the resignations of seven. The membership at the present time consists of 7 honorary members, 461 fellows and 925 members, making a total of 1393.

By unanimous vote the Society adopted the following resolution which had been favorably reported by the Council:

Resolved: That the American Physical Society believes that it is inimical to the progress of American science and to the development of American industry to curtail the privilege of duty-free importation of books and scientific apparatus which educational institutions have heretofore enjoyed under all administrations.

The regular scientific program consisted of seventy-seven contributed papers, nine of which were read by title. The abstracts of all papers will be found on the succeeding pages. The program was as follows:

The State of Polarization of Light Diffracted at Large Angles from Straight Edges of Different Material. J. M. KUEHNE, University of Texas.

An Experimental Method for Determining Quantitatively Under Given Conditions, the Relative Influence of Radiation and Convection in the Transfer of Heat Through Moving Air. L. H. NICHOLS, McGill University. (Presented by A. N. Shaw.)

Geometrical Proof for the Wadsworth Constant-Deviation System. R. C. GIBBS and J. R. COLLINS, Cornell University.

A Piezo-Electric Method for Generating Electric Oscillations of Constant Frequency. W. G. CADY, Wesleyan University.

The Dissipation of Heat in Air from Plain and Blackened Brass Surfaces for Moderate Temperature Differences. T. S. TAYLOR, Westinghouse Electric & Manufacturing Company.

Radiation Equilibrium in an Opaque Uniformly Heated Solid and Duane's Hypothesis as to its Origin. A. G. WORTHING, Nela Research Laboratories.

An Increase in Density in Thin Films. ELIZABETH R. LAIRD, Mount Holyoke College.

Electrical Resistance of a Rotating Coil. A. P. CARMAN, University of Illinois.

The Departure from Ohm's Law in Gold and Silver at High Current Densities. P. W. BRIDGMAN, Harvard University.

Mutual Impedances of Grounded Circuits. GEORGE A. CAMPBELL, American Telephone and Telegraph Company.

Contact Electromotive Forces Due to Films on Metallic Surfaces. A. E. HENNINGS, The University of British Columbia.

Resistance and Thermo-Electric Power of Metallic Germanium. C. C. BIDWELL, Cornell University.

The Production of an E.M.F. on Closed Circuit, by a Light Effect on Argentite. H. HORTON SHELDON and PAUL H. GEIGER, University of Michigan.

Demonstration of the Wind in the Corona Discharge. JAKOB KUNZ, University of Illinois.

Increased Ionization Over Solar Faculae. CHARLES E. ST. JOHN, Mount Wilson Solar Observatory.

A Note on Missing Spectra. A. S. EVE, McGill University.

The Ultra-Violet Absorption of Anthracene and Benzene. J. M. HYATT, Cornell University.

The Ultra-Violet Transmission of Boiled Absolute Ethyl Alcohol. W. R. ORNDORFF, R. C. GIBBS and M. SCOTT, Cornell University.

The Absorption by Water Vapor of Radiation of Wave Lengths Near 6 μ. W. W. SLEATOR and E. R. PHELPS, University of Michigan.

The Infra Red Absorption Spectra of Diatomic Gases and their Ionization Potentials. EDWIN C. KEMBLE, Harvard University.

The Effect of Certain Dissolved Substances on the Infra Red Absorption of Water. J. R. COLLINS, Cornell University.

The Absorption Spectrum of Hydrogen Chloride at 200° K. B. J. SPENCE and C. HOLLEY, Northwestern University.

Two New Lines in the Aluminum Spectrum and their Possible Series Relations. G. D. SHALLENBERGER, University of Chicago.

The Aspherical Nucleus Theory Applied to the Principal Series of Helium. LUDWIK SILBERSTEIN, Eastman Kodak Company.

A Physical Explanation of the Action of the New Singing Tube. CHAS. T. KNIPP and JAKOB KUNZ, University of Illinois.

Theory of Acoustic Wave Filters: The Limiting Frequencies of Transmission. G. W. STEWART, The State University of Iowa.

Diffraction Effects in Sound Absorption Measurements. PAUL E. SABINE, Wallace Clement Sabine Laboratory.

Analysis of the Energy Distribution in Speech. I. B. CRANDALL and DONALD MACKENZIE, Western Electric Company.

The Separation of the Element Chlorine into Isotopes (Isotopic Atomic Species). WILLIAM D. HARKINS and ANSON HAYES, University of Chicago.

On the Determination of Surface Thermal Conductivities. LETHA A. SMITH, McGill University. (Presented by A. N. Shaw.)

The Causes of Reaction Expansion in Amalgams. ARTHUR W. GRAY, The L. D. Caulk Company.

The Porous Plug Coefficient for Air. J. R. ROEBUCK, University of Wisconsin.

Ether-Drift Experiments at Mount Wilson Observatory. DAYTON C. MILLER, Case School of Applied Science.

Photo-Elasticity or Optical Investigation of Stress Distribution in Solid Bodies. PAUL HEYMANS, University of Ghent, Belgium.

Experiments on the Sign of the Electric Charge Assumed by a Metal Immersed in a Liquid. R. D. KLEEMAN and WILLIAM FREDRICKSON, Union College.

The Analysis of Simple Periodic Curves by a Projection Method with Special References to Estuary Tidal Problems. E. V. HENRY, McGill University. (Presented by A. N. Shaw.)

A Galvanometer Method for Producing at a Distance a Magnified Record of a Mechanical Motion. F. WENNER, Bureau of Standards.

The Influence of Small Variations in the Outlet of a Smooth Brass Tube on the Distribution of Static Pressure When Air is Flowing Through the Tube. T. S. TAYLOR, Westinghouse Electric & Manufacturing Company.

Cohesion and Adhesion. WILSON TAYLOR, University of Toronto.

Progress of Work with the Crystelliptometer on Selenium Crystals. LEROY D. WELD, The State University of Iowa.

The Transmitted Effect in Selenium Crystals. J. C. POMEROY, Bethany College.

Further Experiments on Critical Potentials in Hydrogen. F. L. MOHLER, PAUL D. FOOTE and E. H. KURTH, Bureau of Standards.

Photo-electric Phenomena in Coated-filament Audion Bulbs. R. C. GIBBS and EDNA L. MEACHAM, Cornell University.

The Information Service of the National Research Council. ROBERT M. YERKES, National Research Council.

Power Factors in Radio Circuits. N. H. WILLIAMS, University of Michigan.

"J" Radiation: A Summary. F. K. RICHTMYER, Cornell University.

The Dilemma of the Helium Atom. JOHN H. VAN VLECK, Harvard University.

Moment of Momentum of Magnetic Electrons. E. H. KENNARD, Cornell University.

Theory of Ionization by Cumulative Action. K. T. COMPTON, Princeton University.

A Significant Exception to the Principle of Selection. PAUL D. FOOTE, F. L. MOHLER and W. F. MEGGERS, Bureau of Standards.

The Charge on the Alpha Particle. J. E. SHRADER, Westinghouse Electric & Manufacturing Company.

Radiation from a Group of Electrons. LEIGH PAGE, Yale University.

A Magnetic Fall of Potential Method for Testing Short Bars of Iron. ARTHUR W. SMITH, University of Michigan.

A New Method for the Determination of the Magnetic Susceptibilities of Gases. JAKOB KUNZ and E. C. FRITTS, University of Illinois.

A Sine Galvanometer for Determining in Absolute Measure the Horizontal Intensity of the Earth's Magnetic Field. S. J. BARNETT, Carnegie Institution of Washington.

Results of Comparisons of Instruments for Measuring the Earth's Magnetic Elements. LOUIS A. BAUER and J. A. FLEMING, Carnegie Institution of Washington.

Further Results of Line Integrals of the Earth's Magnetic Force. LOUIS A. BAUER and W. J. PETERS, Carnegie Institution of Washington.

Characteristic X-Rays from Light Elements. A. LL. HUGHES, Queen's University.

Energy Relations Between X- and β-Rays. J. A. GRAY, McGill University.

Positive-Ray Analysis of Zinc and Calcium. A. J. DEMPSTER, University of Chicago.

The Effect of Dissolved Substances on the Deposition of Colloidal Particles from a Solution by Means of an Electric Current. RICHARD D. KLEEMAN, General Electric Company.

The Effective Range of β-Rays. J. A. GRAY and A. V. DOUGLAS, McGill University.

On the Spectrum of the γ-Rays from Radium B and C. ALOIS F. KOVARIK, Yale University.

The Beginning of the K and L Series of X-Rays. F. L. MOHLER and PAUL D. FOOTE, Bureau of Standards.

Secondary X-Rays From Crystals. G. E. M. JAUNCEY, Washington University.

Brightness of Tungsten. W. E. FORSYTHE, Nela Research Laboratories.

The Luminescence of Solidifying Antimony. E. KARRER, Nela Research Laboratories.

The Thermionic Work Function of Tungsten. C. DAVISSON and L. H. GERMER, Western Electric Company.

A Spectroscopic Method for Determining the Effective Temperature of Absorbing and Emitting Molecules. RAYMOND T. BIRGE, University of California.

The Excitation of the Enhanced Spectra of Sodium and Potassium in a

Low Voltage Arc. PAUL D. FOOTE, W. F. MEGGERS and F. L. MOHLER, Bureau of Standards.

The Significance of the $\frac{1}{2}$ Terms in Spectral Series Formulæ. PAUL D. FOOTE and F. L. MOHLER, Bureau of Standards.

A Method for Increasing the Carrying Capacity of a Rheostat. W. E. FORSYTHE, Nela Research Laboratories.

A Transition or Absorption Layer Theory of the E.M.F. of the Voltaic Cell. RICHARD D. KLEEMAN, Union College.

Quantum Theory of Photographic Exposure. LUDWIK SILBERSTEIN, Eastman Kodak Company.

The Physical Constituents of the Atmosphere of Venus. CHARLES E. ST. JOHN and SETH B. NICHOLSON.

The Separation of Mercury into Isotopes. WILLIAM D. HARKINS and R. S. MULLIKEN.

The Crystal Structure of Mercury. L. W. MCKEEHAN and P. P. CIOFFI.

The abstracts of the papers on the above program are given in the following pages.

DAYTON C. MILLER,
Secretary.

THE STATE OF POLARIZATION OF LIGHT DIFFRACTED AT LARGE ANGLES FROM STRAIGHT EDGES OF DIFFERENT MATERIAL.

BY J. M. KUEHNE.

THE light diffracted at considerable angles (5° to 25° and more inside the geometrical shadow) is of different states and degrees of polarization according to (*a*) the angle of diffraction, (*b*) the "sharpness" of the edge, and (*c*) the material of the edge. To avoid the influence of "sharpness" (which affects principally the amount of diffracted light under otherwise identical conditions) thin plates of uniform thickness (.15 mm.) and carefully rounded edges were used.

Part of the spectrum from a carbon arc was polarized at an azimuth of 45° and focused on the diffracting edge, which was mounted coincident with the axis of a spectroscope. The diffracted light was examined by means of a long focus microscope which was mounted in place of the telescope, and focused on the diffracting edge. The microscope was equipped with an analyzing nicol and a quarter wave plate.

Dielectric diffracting edges produce a rotation of the plane of polarization of from 0° to 8° or 10° for diffracting angles varying from 0° to 20° or 25° inside the geometrical shadow; the electric vector perpendicular to the edge being the stronger.

Metallic diffracting edges produce very marked elliptical polarization, being distinguished in this respect from dielectric edges. This shows that the vector parallel to the edge, in addition to being more absorbed, is retarded in phase, relative to the vector perpendicular to the edge. This phase retardation varies with different metals and increases with the diffraction angle.

Of the metals so far investigated nickel, aluminum and iron have shown this effect most strongly. In the case of nickel at a diffraction angle of 25° the phase retardation is as much as 90°.

More complete data covering a wider range of materials will be published shortly.

UNIVERSITY OF TEXAS,
AUSTIN, TEXAS,
December 9, 1921.

AN EXPERIMENTAL METHOD FOR DETERMINING QUANTITATIVELY UNDER GIVEN CONDITIONS, THE RELATIVE INFLUENCE OF RADIATION AND CONVECTION IN THE TRANSFER OF HEAT THROUGH MOVING AIR.

BY L. H. NICHOLS.

BY using a pair of slightly modified kata-thermometers,[1] it has been found that the influences of incident heat radiation and of turbulent atmospheric conditions on the transfer of heat to a given place of observation, can be estimated separately and quantitatively over a considerable range of conditions. The experimental procedure consists fundamentally in sorting out these factors by means of their influence on the rate of cooling of previously calibrated models for which the kata-thermometers will serve very conveniently.

Four main operations are necessary; the first of which will suffice indefinitely for the particular instrument calibrated.

1. The preliminary calibration consists primarily of the determination in vacuo, and again in stagnant air of the rates of cooling of the katas (or particular instruments used) when surrounded by large dark enclosures and over the range of temperatures subsequently to be investigated.

2. At the place of testing, the rate of cooling of an ordinary dry kata is obtained in the usual manner.

3. Simultaneously or under similar conditions, the rate of cooling of a dry kata which has been silvered and polished is observed.

4. The apparent temperature of the air is taken by means of a screened thermometer at the place of observation.

By applying the results of previous calibration it is possible to express the quantities measured in terms of units of heat flowing per unit of time. Also by the process of subtraction it is possible to obtain from the results of these operations (1) the influence of incident radiation which arises from sources at higher temperature than that of the surrounding air; (2) the influence of any existing wind, ordinary ventilation, or turbulence as distinct from that of convection in still air.

The validity and practical applicability was tested satisfactorily in the

[1] Hill, Griffith and Flack, "The Measurement of the Rate of Heat-loss at Body Temperature by Convection, Radiation and Evaporation." *Phil. Trans. Roy. Soc.*, B, Vol. 207, p. 201 (1915).

following manner. Readings as outlined above in 2, 3, and 4 were taken in a dark room in the direct paths of radiation from an electric heater, and of wind from a fan, and it was possible by means of these observations and previous calibrations, to predict successfully the readings corresponding to the cases when either the heater or the fan or both of them were removed.

The applications of this method are numerous. In particular it should be possible to allow completely for the influence of solar radiation and atmospheric turbulence upon the readings of various instruments which are at present considered unreliable under open air conditions. The comparative analysis of heating by radiation and heating by convection has important physical bearings and may be facilitated by measurements of this kind.

McGill University.

Geometrical Proof for the Wadsworth Constant Deviation System.

By R. C. Gibbs and J. R. Collins.

By an analytical method Wadsworth,[1] determined the location of the axis of rotation of a constant-deviation prism-mirror system such that the emergent ray remains fixed in position as the system is rotated. This proof involves a series of long though simple transformations.

The location of this axis can be determined by a short geometrical proof similar to that used by E. Bloch,[2] in finding the corresponding axis of rotation for a constant deviation prism of the Pellin-Broca type.

Cornell University,
December, 1921.

A Piezo-Electric Method for Generating Electric Oscillations of Constant Frequency.

By W. G. Cady.

In a former communication[3] several methods were described whereby the frequency of a vacuum-tube oscillating circuit could be rendered very stable by the use of a piezo-electric resonator of proper dimensions. Further investigation has shown that it is possible, with the aid of amplifiers, to make the piezo-electric resonator serve as a *mechanically tuned feedback*, so that a high-frequency alternating current is generated, whose frequency is determined solely by the mechanical vibrations of the quartz plate. The plate is so mounted as to vibrate freely longitudinally between two pairs of close-fitting metallic "coatings." The first pair of coatings is connected between the output anode of a three-stage resistance amplifier and ground, while the second pair is connected between the input grid and ground.

[1] Astronomy and Astro Physics, Vol. 13, p. 835, 1894.

[2] Journal de Physique, Vol. 7, p. 145, 1917.

[3] Physical Review, 18, p. 142, 1921. A more complete account of these experiments, together with the theory of the piezo-electric resonator, will appear in the Proceedings of the Institute of Radio Engineers.

Any slight increase in potential of the output anode alters the electric field between the first pair of coatings, and sets the resonator into vibration. The charges thereby excited in the second pair vary the potential of the input grid. This varying potential, by virtue of the amplification taking place in the system, will, if the proper coating is connected to the grid, still further increase the potential variations of the output anode and thus maintain the vibrations of the resonator. The power output is of course very small—of the order of 1/20 watt—but this small power may of course be further amplified. Maximum power is obtained by tuning the output circuit by means of a variable condenser and inductance in parallel. If the resonator functions properly, however, the frequency is found to be practically independent of the electrical constants, the current merely passing through a maximum when in electrical resonance. The forced vibrations which the resonator executes have a frequency which is not entirely without influence from external circumstances; yet it hardly ever differs from the natural frequency of the resonator by more than one part in 10,000, and for wide ranges of the various parameters of the circuit the variation is very much less than this.

By the use of quartz plates 3 cm. long, frequencies of (roughly) either 100,000 or 200,000 may be obtained. I have not yet succeeded in obtaining regeneration with frequencies much higher than these. For frequencies so low that it is impracticable to use quartz plates of sufficient length, flat steel rods have been successfully employed. Such a rod has a small quartz plate cemented to each side at its center, and each of the quartz plates is provided with two separate tinfoil coatings. In this case a five-stage amplifier has been found necessary for regeneration. The frequency is essentially that of the steel rod, the quartz plates serving merely to excite longitudinal vibrations in the steel.

WESLEYAN UNIVERSITY,
MIDDLETOWN, CONN.

THE DISSIPATION OF HEAT IN AIR FROM PLAIN AND BLACKENED BRASS SURFACES FOR MODERATE TEMPERATURE DIFFERENCES.

BY T. S. TAYLOR.

OBSERVATIONS have been made in air, free from convection currents other than those set up by the apparatus itself, of the loss of heat from a flat heater when its surfaces were plain brass and when blackened, for various temperature differences and angular positions relative to the vertical. The energy put into the heater was varied till temperature excesses of the heater's surface were obtained up to 130° C. The surface temperatures were obtained by small copper-constantan thermocouples peened into the metal surface. By temperature excess is meant the difference between the temperature of the heater and that of the surroundings and in particular that of the air before it came into the field of influence of the heater.

Assuming black body radiation for the blackened surface, the heat losses

for various temperature differences were calculated for both radiation and convection. For a temperature difference of 100° C., the following relative values were obtained for the different losses per unit area.

1. Total loss from blackened surface	100
2. Total loss from plain brass surface	55.5
3. Loss due to radiation alone from blackened surface (assuming black body radiation)	62.7
4. Convection loss alone. (This is assumed the same for both surfaces for the same temperature difference)	35.8
5. Difference between blackened and plain	44.5
6. Radiation alone from brass surface	17.1

The differences obtained between the losses from the heater used $8\frac{3}{4}'' \times 8\frac{3}{4}'' \times \frac{3}{4}''$ when placed at various angles were practically no greater than those due to experimental variations. This is true also concerning the differences between the temperatures of the heater surfaces.

Westinghouse Research Laboratories.

Radiation Equilibrium in an Opaque Uniformly Heated Solid and Duane's Hypothesis as to its Origin.

By A. G. Worthing.

Whether or not the *natural radiation* from the ultimate sources of radiation in an opaque uniformly heated solid agrees in spectral distribution with the *equilibrium radiation* in their immediate neighborhood depends on the optical constants of the solid. The condition for agreement is constancy in κ/λ, where κ (often written nk) is the extinction coefficient and λ the wave-length in vacuo. A considerable tendency toward constancy exists in the measured values of this ratio. Possibly the variations found are real but analogous to those experienced in atomic heats in their relation to Dulong and Petit's law. Whatever the explanation, known difficulties due to surface transition layers seem to justify a tentative assumption of constancy for the purpose of testing theories of the origin of radiation.

Duane's hypothesis, a generalization from X-ray observations, ascribes all radiation to the bombardment of atoms by moving electrons—in the ordinary temperature radiations of incandescent solids, the free electrons connected with electric conduction. Starting with three fundamental assumptions, Duane concluded that Planck's distribution law results. Apparently, however, he overlooked the fact that the coefficient A in his statement of Maxwell's law is in general a function of temperature. Fortunately, however, thermionic emission experiments seem to indicate that the concentration of the free electrons in a solid varies in such a fashion, at least for low concentrations and high temperatures if not in general, as to render the coefficient A constant for this special case.

It is to be inferred from Duane's derivation that the natural radiation from the ultimate sources has the characteristics of black body radiation for free

space. This is almost certainly not the case. Black radiation in free space differs from the equilibrium radiation in an opaque solid, and only in case κ/λ is constant as stated above, has this equilibrium radiation the same spectral distribution as the natural radiation from the ultimate sources. Assuming the constancy of κ/λ and thus for the natural radiation the same spectral distribution as for equilibrium radiation, it seems necessary to modify Duane's assumption (3) so as to read "*the energy radiated per hit is on the average proportional to the fourth power of the speed of the free electron and to the square of the index of refraction for the radiation emitted.* In other words,[1] *the ratio of the energy radiated per impact to the kinetic energy of the impacting electron is proportional on the average to the square of the ratio of the velocity of propagation of the radiation in the solid to that in vacuo.* On the new basis Planck's equation follows without question as to applicability.

In addition to giving certain indications regarding the application of Maxwell's law to free electrons, and pointing out the possibility of a constancy in κ/λ, the discussion shows how Duane's hypothesis, when combined with an assumption of such constancy and with conclusions arrived at independently in other lines of research, gives a satisfying physical concept of processes which may underlie the emission of radiation by its ultimate sources.

NELA RESEARCH LABORATORIES,
NELA PARK, CLEVELAND, OHIO.

AN INCREASE IN DENSITY IN THIN FILMS.

BY ELIZABETH R. LAIRD.

SOME phenomena noted while working with thin celluloid films seemed to indicate that the weight was not proportional to the thickness as determined by an interferometer. Since a number of observers give the thickness of similar films without details as to method of determination, it was decided to investigate the point. For this purpose it was necessary to measure the index of refraction of films of various thickness, the displacement of fringes in an interferometer, the area of the films, and their weight.

It was attempted to measure the index of refraction by a critical angle method by depositing a thin film directly on one side of a glass prism, or by using it as one side of a thin cell with carbon bisulphide as the liquid in between. As far as it went this method indicated no change in the index of refraction with increasing thinness, but in the first case the films made perfect contact with the glass only in little spots, and in the second such a small amount of light was refracted into the prism that an accurate setting with a spectrometer was impossible. The method of using the polarizing angle for this determination proved very convenient, as the same film could be used in this as in the other measurements. The index of refraction found thus showed very little change if any from thick films down to the thinnest used. The index found was between 1.50 and 1.51.

[1] As reworded by the writer's colleague, Dr. E. Q. Adams.

The optical thickness was measured by the fringe displacement in a small Michelson interferometer by noting first the displacement of the central black fringe in white light, then changing to sodium light and noting the displacement of a number of fringes for different positions of the film in order to get an average thickness. The area of the films was found by measuring with a planimeter the hole from which they were cut. The early weighings were made on an ordinary balance sensitive to 0.05 mg., the later by observing in a tele-microscope the displacements of a glass thread clamped at one end and suitably protected from draughts, when the films were placed in a stirrup forming part of the thread. With this weighings could easily be made to 0.005 mg.

The later results were in general agreement with the earlier, and assuming the optical thickness as the true thickness, show that while the density down to a thickness of 400 $\mu\mu$ remains approximately 1.41 grams per cm.^{3}, somewhere below this it begins to increase so that in the neighborhood of 60 $\mu\mu$ it is about 2 and at 30 $\mu\mu$ about 2.5 and that it is higher still at smaller thicknesses. It is expected to continue the experiments.

Mount Holyoke College.

Electrical Resistance of a Rotating Coil.

By A. P. Carman.

The coil is wound on a circular disk and the disk is rotated at a high speed about its axis. The centrifugal force is thus at right angles to the wire, and if "the electric current has a true momentum" (using Maxwell's words), it might be forced to the outer part of the cross-section of the wire. The experiment is made to determine if this cross-centrifugal force produces any change in the electrical resistance of the coil. The experiment was made in 1913–1914,[1] but gave no results because of a lack of a satisfactory means of making electrical connection with the rotating coil. A year ago a successful method of connecting with such a moving coil was devised;[2] this was described in a paper before this Society at the preceding, Chicago, meeting. From the center of each end of the shaft a fine wire is stretched in the line of the axis of the shaft extended. The wire is about 25 centimeters long and ends in a small swivel and a spring to keep the wire straight. The wire can thus rotate with the shaft, and even when the shaft is totating at 7,000 r.p.m. for considerable time, there is little twist in this axial connecting wire. The wire runs through a mercury trough, passing loosely through end corks, and connection to the outside circuit is made by means of the mercury. To avoid thermo-electromotive forces, connection to the coil was not made through the shaft, but through an insulated tapered plug, and then by an insulated wire which was carried through a hole along the axis of the shaft. Potentiometer tests

[1] Thesis of P. L. Bayley, June, 1914, MS. in University of Illinois Library.

[2] Thesis of C. C. Schmidt, 1921.

showed that the thermal e.m.f.'s in the circuit were less than two millionths of a volt, that is, were negligible. The coil on the disk can be quickly cut out by a short-circuit, and thus the resistance changes in this connection can be measured and allowance made for it. These resistance changes between conditions of rest and of rotation were, under normal conditions, thousandths of an ohm or less, and the changes were not greater for high speeds. The following are random examples of these resistance changes.

	Ohms.				
R. at rest	.1248	.1244	.0733	.0724	.0729
R. rotating	.1323	.1312	.0724	.0729	.0731
Difference	.0075	.0068	.0009	.0005	.0002

A disk wound with copper wire was the first one prepared, but it was found to be so sensitive to temperature effects that all other resistance changes were masked. The next disk was wound with "advance" wire, this wire having a negligible temperature coefficient for resistance. The disk was turned from vulcanized fiber one inch thick, and twenty-eight layers of No. 25 wire were wound in a groove on the circumference and covered with a layer of sealing wax. The average diameter of the coil was 28 cm. Around the edge of the disk, and over the coil was clamped by brass straps a stout hickory band which had been steamed and formed into a circle. For the final experiments, a steel hoop was fitted over the hickory band. The shaft was mounted on "S.K.F." ball bearings and was driven by a long belt from a two-phase induction motor with step-up pulleys. The resistance of the coil at rest was 235.838 ohms, and at 6,837 r.p.m. the resistance was 236.128 ohms, showing an increase of 0.29 ohm or over one tenth of one per cent. increase after allowing for connection changes. This increase and the increases of resistances at speeds of 1,450, 1,960, 2,450 and 4,960 r.p.m. were exactly proportional to the squares of the speeds, and were evidently due to centrifugal forces. Calculations using the ordinary elastic constants of steel were made for the stretch of the steel binding hoop at the highest speed, this being the limiting stretch of the coil. Assuming that the increase of resistance is proportional to the stretch for these small stretches, it was found that the observed increase of resistance was due in considerable part, if not wholly to stretch. But there were some differences and more decisive results were sought. Hence a coil was prepared with loose zigzag windings. With this arrangement, the wire can straighten itself without change of length and hence without strain, when the binding hoop stretches under centrifugal force. With this new coil the change of resistance from rest to a speed of 7,000 r.p.m. was less than one hundredth of one per cent., and probably not over one thousandth of one per cent. The actual resistance measurements were: at rest, 270.4148 ohms; at 6,934 r.p.m., 270.4176 ohms; at 5,199 r.p.m., 270.4231; or the differences were in the

thousandths of an ohm, probably due to the connections. The diameter of the coil was 28.8 cm., so that tangential speed was about 10 kilometers per second, and v^2/r, the acceleration, was about 4×10^7 cm. per sec. per sec. We conclude that if there is any change of the electrical resistance of this wire due to centrifugal force, the change is exceedingly small.

University of Illinois,
December, 1921.

The Departure from Ohm's Law in Gold and Silver at High Current Densities.

By P. W. Bridgman.

Previous attempts to detect a deviation from Ohm's law in metals at high current densities, which is to be expected from electron theory, have failed. The chief source of error in previous measurements has been the uncertain correction for the change of resistance under the heating due to the heavy current. A new method has been developed in which this source of error is absent. The method consists of measuring the resistance simultaneously under a heavy direct current and a small superposed alternating current of acoustical frequency. If Ohm's law fails the resistance to the direct current will be different from that to the alternating current. It is obvious that the large temperature error of previous methods is absent because the temperature is the same to direct and alternating current. There is another source of error, however, due to the small alternations of temperature under the joint action of direct and alternating current. This error becomes vanishingly small at high frequencies, and may be eliminated by making measurements at a number of frequencies and extrapolating to infinite frequency. The extrapolation is secured by a knowledge of the theoretical form of the curve.

The method has been applied to gold and silver leaf; the thickness of the gold varied from 8×10^{-6} to 2×10^{-5} cm., and the thickness of the silver was 2×10^{-5} cm. Current densities of 5×10^6 amp./cm.^{2} were attained. Under these current densities there is an increase of resistance of the order of one per cent. The increase is greater for the thick than the thin gold, as would be expected, and is greater for gold of the same thickness than for silver.

These experiments mean, if metallic conduction takes place by a mechanism like a free-path mechanism, that the free path is much longer than the distance between atomic centers. This is in accord with the theory of metallic conduction which I have previously advanced.

The Jefferson Physical Laboratory,
Harvard University, Cambridge, Mass.

Mutual Impedances of Grounded Circuits.

By George A. Campbell.

An investigation is being made of the mutual impedances between grounded circuits. In case the frequency and separation do not exceed specified limits,

it has been shown that a good first approximation is obtained by using formulas for the direct current mutual resistance and mutual inductance. Any network of conductors located on the surface of the earth with which it is conductively connected at any number of points will, for direct currents, have self and mutual inductances which are equal to the Neumann integral, extended over the network alone. In other words, that portion of the complete Neumann integral for closed circuits which involves the return currents through the earth, vanishes. The earth is assumed to be flat, of infinite extent, of unit permeability and of uniform conductivity.

AMERICAN TELEPHONE AND TELEGRAPH COMPANY.

CONTACT ELECTROMOTIVE FORCES DUE TO FILMS ON METALLIC SURFACES.

BY A. E. HENNINGS.

IN preliminary experiments preparatory to an investigation of the temperature coefficient of contact electromotive forces between metallic surfaces certain new phenomena have been observed which indicate that the true effect may be completely masked by the formation of films.

The experimental arrangement was such that one of the surfaces could be changed through a wide temperature range, while the other was not changed in temperature, except in so far as this was brought about by radiation from the first surface. The bottom of a brass cylinder projecting into the vacuum chamber served as the first of these surfaces and the second was that of an insulated brass plate in communication with a quadrant electrometer. By means of an electro-magnetic device this latter plate was brought near or away from the bottom of the cylinder. Thus the Thomson method of measuring the contact electromotive force could be applied.

When liquid air was poured into the cylinder and when the vacuum was such as could be obtained with a Gaede mercury pump, but without charcoal absorption, the contact electromotive force between the brass surfaces changed rapidly from + .02 volt at 20° C., to a higher positive value, which changed quickly to a negative value reaching a maximum of − .78 volt. After the liquid air had evaporated and the bottom of the cylinder began to rise in temperature, the contact electromotive force changed, comparatively slowly at first, to a less negative value, but then very abruptly from − .47 volt to + .32 volt between the times of two observations made as quickly as possible. A maximum of + .43 volt was reached in a short time, which, however, gradually fell, approximating the initial value when the whole apparatus approached the temperature of the room. Other series of observations yielded still greater differences between extremes, the total change in one case being between + .28 and − 1.13 volts.

With an improved vacuum the fluctuations were less pronounced, but nevertheless such that no data, purporting to represent the true temperature coefficient of contact electromotive forces, were obtained.

UNIVERSITY OF BRITISH COLUMBIA.

Resistance and Thermoelectric Power of Germanium.

By C. C. Bidwell.

The electrical resistance and the thermoelectric power of a sample of very pure metallic germanium have been determined, simultaneous data on the two properties having been taken from −192° C. to +675° C. A reversible transformation of some sort is indicated by the data. The change begins at about +125° C. and is apparently not completed until at least 550° C. is reached. The thermoelectric power is positive with a positive temperature coefficient from −192° C. to +125° C., the value being approximately +160 microvolts at −192° C. and +425 microvolts at +125° C. With further temperature rise the thermoelectric power diminishes rapidly, changing sign at 300° C. It becomes again a linear function of the temperature from 550° to 675° with a positive coefficient, the value at 550° being about −175 m. v. and at 675°, −125 m. v.

The resistance shows a minumum at —116° C. with a positive temperature coefficient from that temperature to +125°. It goes through a maximum at about +175° C., thereafter dropping with rising temperature to a minimum at +645°. The resistance-temperature law between − 193° and +125° and from 550° to 675°, *i.e.*, where not obscured by the transformation, is of the form $\log R = \alpha/T + \beta T + \gamma$. This is the law which has been shown to hold for many of the oxides and non-metals.

In the transition region there seems to be a solid solution of one form in the other, the relative proportions depending upon the temperature.

The Production of an E.M.F. on Closed Circuit, by a Light Effect on Argentite.

By H. Horton Sheldon and Paul H. Geiger.

While obtaining data on the change of resistance of argentite (Ag_2S) with change of illumination, it was observed that under certain conditions a deflection of the galvanometer was secured on illumination when no external e.m.f. was applied to the circuit. This effect was further studied when the crystal was connected directly to the galvanometer and the direction of the e.m.f. found to depend upon the contact illuminated.

When the lamp was replaced by a heating coil, which radiated a much greater amount of heat than the lamp by a thermopile test, certainly less than one per cent. of the deflection was secured, thereby showing that a true light effect was being obtained. Other experiments resulted in the same conclusion.

The effect of intensity was studied by varying the distance between lamp and crystal and it was found that the e.m.f. produced decreased with distance. With one crystal an e.m.f. of .0125 volt was obtained with a 20-candle power lamp at 12 cm. from the contact. The procedure was complicated by a changing resistance in the crystal.

This light effect was found in over a dozen specimens secured from different regions, as well as in a number of other minerals. However, the effect was more marked in argentite than in any of the other crystals examined.

It was found that the resistance of a crystal of argentite varied from several megohms with a potential difference across the crystal of one volt to less than a hundred thousand ohms with a potential difference of twenty volts. In obtaining the curve showing this relation, it was found necessary to apply the voltage only for a very small fraction of a second for the resistance very rapidly increased with the time that the voltage was applied.

The ratio $\Delta R/R$ (ΔR being the change of resistance on illumination) was found to be a constant for different applied voltages.

UNIVERSITY OF MICHIGAN.

DEMONSTRATION OF THE WIND IN THE CORONA DISCHARGE.

BY JAKOB KUNZ.

THE wind has been demonstrated by means of vapors of ammonium chloride and ether. The deflections of these vapor jets can easily be projected on a screen by means of an arc lamp without lenses. A corona discharge of alternating currents between 2 parallel wires of different diameters has been used. The phenomena presented by 2 different and 2 equal wires are very different.

UNIVERSITY OF ILLINOIS.

INCREASED IONIZATION OVER SOLAR FACULÆ.

BY CHARLES E. ST. JOHN.

ON the Bohr theory, radiation of the normal or arc-type occurs when the nuclear charge is unity and an electron falls from an orbit to one of lower potential energy. The enhanced or spark lines are produced when the nucleus is doubly charged and the atom is first-step ionized. Saha has adapted the Nernst equation for the equilibrium of gaseous reactions to the determination of the percentage of ionized to un-ionized atoms as a function of temperatures and pressure. The Saha equation suggests, as he points out, that in the spectra of faculæ, owing to higher temperature, the percentage of ionization should be increased and hence the enhanced lines strengthened. Preliminary spectrograms of faculæ show changes in the intensity of the enhanced lines in agreement with this deduction, the spectrum changing from Go to F-type, that is in the direction of higher temperature. The preliminary results for titanium are as follows:

Wave-length.	Class of Line.	Effect over Faculæ.
4306.078	Arc	No change
4443.976	Spark	Strengthened
4468.663	Spark	Strengthened
4501.445	Spark	Strengthened
4548.198	Arc	No change
4527.490	Arc	No change
4572.156	Spark	Strengthened

Mount Wilson Solar Observatory.

A Note on Missing Spectra.

By A. S. Eve.

Mining engineers use well-constructed sieves made of phosphor bronze wire with various sizes of mesh, ranging up to three hundred wires to the inch. When a narrow beam of parallel light falls on the sieve diffraction bands and patterns are produced which may be observed directly, or after projection. By a calculation involving simple proportion only, the wave-length of any light can be determined.

A sieve with 300 wires to the inch was found to have the intervals between the wires precisely equal to their diameters. It necessarily follows that the even order spectra are entirely absent, while the odd order spectra are enhanced in brilliancy. On inclining the sieve to the ray the gaps are effectively narrower while the circular wires are not, hence at about 30° the missing spectra suddenly appear.

A photograph of the sieve was taken with a white screen behind it. This photograph was used as a grating and all the spectra were found present. Possibly the light flooded the plate when the photograph was taken, so that the gaps were enlarged relatively to the image of the wires. There is no new principle involved in the above, but the method is a valuable and effective method of demonstrating missing spectra. Such sieves might have advantages over coarse gratings in astronomical work.

McGill University.

The Ultraviolet Absorption of Anthracene and Benzene.

By J. M. Hyatt.

The purpose of this investigation was to check the results previously obtained, by using the Hilger sector photometer according to the method described by Howe.[1]

Anthracene.

The anthracene absorption was determined by using a number of different concentrations of the anthracene in ethyl alcohol, the thickness of the absorbing

[1] H. E. Howe, Phys. Rev., Vol. VIII., 1916.

layer being 1 centimeter in each case. Ten absorption bands were observed, four of them however were too faint to admit of quantitative measurements of the absorption coefficient. The four intense bands were double, the secondary bands being distinctly visible on the photographic plate.

The figures in the table give the frequency numbers of the absorption bands together with those obtained by Hartley[1] and by Glatzel.[2]

It may be seen from Table I. that there is an approximately constant interval of 150 in the frequencies between the first, third, fifth, etc., bands and an interval of approximately 140 between the second, fourth, etc., bands. The fourteen bands may be represented by two series, series A with a mean frequency interval of 147; and a series B with a mean frequency interval of 142. The third and fourth bands in the table were taken as references and two series were computed with an interval of 147 and 142.

TABLE I.

Hartley	Glatzel.	Observed.	Computed.
2,635	2,620	2,650	2,653
	2,680	2,700	2,698
2,780	2,780	2,800	2,800
	2,840	2,840	2,840
2,915	2,965	2,945	2,947
	3,025	2,990	2,982
3,050	3,100	3,095	3,094
		3,130	3,124
		3,240	3,241
			3,266
			3,388
		3,410	3,408
		3,540	3,535
			3,550
			3,682
		3,688	3,692
			3,829
			3,834
		3,975	3,976
			3,976
			4,123
		4,115	4,118

Benzene.

The absorption of the benzene was determined, using very thin layers of the solutions of benzene in ethyl alcohol. Ten absorption bands were observed, three of them being however very faint.

The position of the ten bands that were found are compared in the Table II. with the position of those that were found by previous observers.

[1] Hartley, Journal Chem. Soc., Vol. 39, 1881.

[2] Glatzel, Physikalische Zeitschrift, Vol. 2, 1900.

Table II.

Hartley and Dobbie.[1]	Glatzel.[2]	Baly and Collie.[3]	Observed.
3,710		3,725	3,720
		3,765	3,780
3,833	3,820	3,830	3,830
3,925	3,920	3,915	3,920
4,014	4,010	4,025	4,015
4,109	4,110	4,110	4,120
4,205	4,200	4,200	4,210
			4,295
			4,365
			4,465

Cornell University,
December, 1921.

The Ultraviolet Transmission of Boiled Absolute Ethyl Alcohol.

By W. R. Orndorff, R. C. Gibbs and M. Scott.

In measuring the ultraviolet absorption spectra of two isomers of a certain organic salt when dissolved in absolute ethyl alcohol, it was found that the absorption of a solution of either isomer changed gradually on standing in such a way as to indicate a slow transformation to the other isomer. Although the absorption spectra of the two solutions differed widely when first made up, at the end of six months the absorption of the two had become almost identical.

In attempting to modify the equilibrium thus established between the two isomers in solution, one of the solutions was heated to the boiling point. The absorption of the solution after heating showed that instead of simply changing the ratio of the two isomers the heating had modified the solution in other ways. One possible explanation of the change was that the *solvent* had been modified in some way. The transmission of boiled absolute alcohol was therefore measured and compared with that of freshly distilled absolute alcohol. It was found that for a layer 1 cm. thick the transmission of the boiled alcohol was decidedly less than that of alcohol which had not been heated after distillation from about 0.37 μ to about 0.24 μ (the shortest wave-length studied). The maximum decrease in ratio of transmission for 1 cm. layer was about 90 per cent.

The decrease in transmission increases with the time of boiling up to a certain point. Within small limits the change in transmission is the same for alcohol boiled in flasks made of ordinary glass, pyrex glass, or Jena glass, or in a nickel-plated copper flask. In all these cases the vapor produced by

[1] Hartley and Dobbie, Journal Chemical Soc., 1898.

[2] Glatzel, Physikalische Zeitschrift, Vol. 2, 1900–01.

[3] Baly and Collie, Journal Chemical Society, 1905.

boiling was condensed and returned to the flask. The transmission increases slightly for a few days after the alcohol is boiled. The alcohol condensed from the vapor produced by boiling gave the same transmission as the unboiled alcohol.

It is quite possible that the change in transmission here described is not due to any real change in absorption but to a scattering produced by colloidal particles of the material of the flask or to oxidation of the alcohol.

It is hoped that in the near future experiments can be performed to determine whether scattering or oxidation is the cause of the change in transmission. Similar changes, although somewhat less marked, were found for boiled water and boiled glacial acetic acid.

CORNELL UNIVERSITY,
December, 1921.

THE ABSORPTION BY WATER VAPOR OF RADIATION OF WAVE-LENGTHS NEAR 6 μ.

BY W. W. SLEATOR AND E. R. PHELPS.

THE study of the absorption spectrum of water vapor undertaken a few years ago has been continued, and the analysis of the region of 6 μ has been completed. The new map shows a more complicated structure than was presented before, and proves the existence of many individual lines hitherto only suspected or quite unknown. It is plain however that the number of known lines would be still further increased by higher dispersion. The interest of the work lies in its bearing on the theory of band spectra, the information it supplies about possible series in the water vapor spectrum and the help it may give in problems of molecular structure.

UNIVERSITY OF MICHIGAN.

THE INFRA-RED ABSORPTION SPECTRA OF DIATOMIC GASES AND THEIR IONIZATION POTENTIALS.

BY EDWIN C. KEMBLE.

THE Lenz[1] theory of the infra-red band spectra of gases is simply the straightforward application to molecular rotational and vibrational motion of the Wilson-Sommerfeld quantum conditions, the Bohr frequency principle, and the Bohr principle of selection. Kratzer[2] has recently derived a formula for the frequencies of the lines in the infra-red absorption spectra of diatomic gases in conformity with the Lenz theory, but his method of evaluating the quantum integral for the vibrational motion is open to objection.[3]

Using a method of integration in series described in a previous paper[3] the writer obtains the following new formula for the frequencies in the infra-red

[1] W. Lenz, Verh. d. D. Phys. Ges., 31, p. 632, 1919.

[2] A. Kratzer, Zeit. f. Phys., III., 5, p. 289, 1921.

[3] E. C. Kemble, Proc. Nat. Acad. Sci., 7, p. 283, Oct., 1921.

absorption spectrum of a diatomic gas:

$$\nu_s{}^n = k_0{}^{(n)} + k_1 s + k_2{}^{(n)} s^2 + k_3 s^3 + k_4{}^{(n)} s^4 + \cdots.$$

Here n, $|s|$ are the vibrational and rotational quantum numbers for the final stationary state, respectively, and 0, $|s \pm 1|$ are the corresponding initial quantum numbers. n is unity for the "fundamental" band, two for the first "harmonic," etc. s is the term number of the line in question reckoned from the component next the center on the red side as zero. The coefficients k_1 and k_3 are independent of n. All the constants are determined in terms of the coefficients in a power series expansion for the potential energy.

The new formula agrees with that of Kratzer for small values of s and n. It may be checked in three ways. There is, in the first place, a definite relation between k_3, k_1, and k_0 which may be verified by an experimental study of these constants. The recent observations of Colby and Meyer[1] on the HCl band at 3.5 μ form a rough, but as yet insensitive check on this requirement of the theory. In the second place, the coefficients k_1 and k_3 should be the same for the harmonic band as for the fundamental. In testing this point the data obtained by Imes[2] for the HCl band at 1.7 μ were used. The agreement is not perfect, but seems to be within the limits of experimental error.

From a sufficiently complete experimental knowledge of the infra-red absorption spectrum of a diatomic gas it is possible by means of this theory to calculate its ionization potential and thus to obtain a third check. The ionization potential of HCl calculated from the available spectroscopic data is 14 volts in close agreement with the experimental vaule obtained by Foote and Mohler[3] and the theoretical value calculated by Born[4]. The spectroscopic data for HBr are neither so complete nor so accurate as for HCl, but a rough preliminary calculation yields an ionization potential of 12 + volts in satisfactory agreement with the value 13.5 volts, computed by Born.

Harvard University,
Cambridge, Mass.

The Effect of Certain Dissolved Substances on the Infra-red Absorption of Water.

By J. R. Collins.

The absorption spectrum of aqueous solutions of inorganic compounds were studied quantitatively to determine the effect of the solute on the absorption of the water. The spectrum was studied from 0.8 μ to 2.3 μ, which range includes four absorption bands of water. The procedure consisted of determining the per cent. transmission of a measured thickness of the solution and of a thickness of pure water equivalent to the amount of water in the solution.

[1] W. Colby and C. F. Meyer, Astrophys. Journ., 53, p. 300, May, 1921.

[2] E. S. Imes, Astrophys. Journ., 50, p. 251, 1919.

[3] Foote and Mohler, J. Am. Chem. Soc., 42, p. 1832, Sept., 1920.

[4] M. Born, Verh. d. D. Phys. Ges., 21, p. 679, 1919.

As the absorption bands vary widely in their intensities four different thicknesses of solution and water were used for various parts of the spectral region studied. The per cent. transmission curves of the solution and water were plotted together for comparison.

Two spectrometers in series were used to insure purity of the spectrum. These were of the constant deviation type with glass prisms and lenses. A Coblentz linear thermopile and iron-clad galvanometer were used to measure the radiation. A very careful determination of the transmission of various thicknesses of water was made, errors due to reflection in the absorption cells being eliminated by using the two cells of different thickness. These cells were placed in turn in the beam passing through the spectrometer system and thus was determined the transmission of a layer of water equal in thickness to the difference in thickness of the two cells. The transmission of the solutions was determined by obtaining the ratio of the transmission of the solution to that of an equal thickness of water.

The spectrometer was calibrated by the use of emission spectra of lithium, sodium, and potassium salts volatilized in the arc and the mercury arc. A very careful determination of the absorption of water was made in the region .8 μ to 2.3 μ. The positions of maximum absorption of water were located at .97 μ, 1.20 μ, 1.44 μ and 2.00 μ, the corresponding coefficients of absorption being .448, 1.22, 29.4 and 103. The coefficient of absorption α is defined by the relation

$$J = J_0 e^{-\alpha t}.$$

J = transmitted radiation, J_0 = incident radiation, t = thickness of absorbing layer.

The materials used as solutes were NaCl, $AgNO_3$, NH_4NO_3, $CaCl_2$, $BaCl_2$, $SrCl_2$, $MgCl_2$, $Mg(NO_3)_2$, $Zn(NO_3)$ $ZnSO_4$, $Al_2(SO_4)_3$, Al_2Cl_6, $Al_2(NO_3)_6$, $Na_2S_2O_3$, NaOH, KOH, LiOH. The first three are non-hydrating substances, while the rest are supposed to combine to a greater or less extent with some of the water in which they are dissolved. The results are masked to a certain extent by the absorption of the dissolved substances, but a decrease in the absorption of the solution from that of an equivalent amount of pure water is evidence of a change in the absorption of the water caused by the solute.

No general rule is found for the behavior of the hydrating substances: $ZnSO_4$, $Al_2(SO_4)_3$, LiOH, NaOH, KOH, increased the transmission of the water in all four absorption bands; the other hydrating substances increased the transmission of the water in the absorption band at 1.44 μ but do not affect the transmission of the water at the other absorption bands in any regular manner. The three non-hydrating substances decrease the transmission of the water in the two absorption bands at .97 μ and 1.2 μ, increase the transmission of the water in the absorption band at 1.44 μ, and do not affect the transmission in the same way at the remaining absorption band. Thus every substance studied increased the transmission of the water in the absorption band at 1.44 μ.

H. C. Jones[1] attempts to explain the effect on the basis of the solvate theory. In his explanation the transmission of the water should be increased in all the absorption bands by the hydrating substances, and should be unaffected by the non-hydrating substances. This explanation cannot fit the present results without some serious modifications.

Cornell University,
December, 1921.

The Absorption Spectrum of Hydrogen Chloride at 200° K.

By B. J. Spence and C. Holley.

Planck[2] assuming that Bohr's static orbits are not the only possible ones (an assumption compatible with the classical laws of electrodynamics) has made a study of the absorption spectrum due to the rotations of electrical doublets with free axes. He finds as one result of this investigation that maximum absorption should occur at the wave length

$$\lambda \max = 2\pi c \sqrt{\frac{J}{KT}},$$

where c is a constant, K Planck's constant, J the moment of inertia of the doublet, and T the absolute temperature.

The investigation is an attempt to verify the above formula. The absorption of the diatomic gas hydrogen chloride was studied at room temperature and also at 200° K., just above its liquefaction temperature (− 83° C.) at atmospheric pressure. This gas shows absorption bands beyond 10 μ which are attributed to molecular rotation. It also shows a series of bands in the region of 3.5 μ which according to Bjerrum (Nernst Festschrift, 1912) are due to the combination of the frequencies of the bands beyond 10 μ with that of the vibration of the molecule. In the application of the Planck expression, we have assumed that any variation in absorption beyond 10 μ will make itself evident as a change in the absorption in the region at 3.5 μ. to which we have confined our study. The investigation was carried on by means of an infra-red spectroscope of the fixed arm type, using a plane grating of 2,500 lines per inch, kindly loaned to us by Professor H. M. Randall of the University of Michigan.

It was found that there was a greater general absorption at the low temperature than at room temperature. In addition, it was found that the bands due to the lower rotational frequencies as evidenced in the 3.5 μ region were very much less pronounced, almost disappearing at the low temperature, while those corresponding to the higher frequencies were not diminished in anything like a similar ratio. It was also found that the number of bands observed remained the same, with no shift in their wave-length at the low temperature.

[1] Phys. Zeit., Vol. 15, p. 447, 1914.

[2] Annalen der Physik, 53, 24, 1917.

At the low temperature we expected on the basis of the Planck expression that the bands due to the higher frequencies of rotation would be less pronounced or decreased in a greater ratio than those due to the lower frequencies. The investigation appears not to confirm the Planck expression for the temperature chosen.

NORTHWESTERN UNIVERSITY.

TWO NEW LINES IN THE ALUMINUM SPECTRUM AND THEIR POSSIBLE SERIES RELATIONS.

BY G. D. SHALLENBERGER.

WHEN a high potential vacuum spark, which has been described by Millikan,[1] is applied to Al electrodes, two unidentified lines are obtained in the spectrum of this element. They are at λ 4150.6 and λ 2907.4 respectively. Both are strong, well-defined lines. The one with the longer wave-length has the higher intensity rating. It is of about the second or third order of magnitude, while the shorter line is of about the fourth or fifth, as compared with the other Al lines. The assigned wave-lengths are probably correct to .3 or .4 of an Ångstrom unit. It is hardly possible that these lines are due to impurities; since elements which have lines near these positions have other stronger lines elsewhere which did not appear on our plates and the lines of the elements which are present as impurities are faint.

While these lines are apparently not to be placed in any of the simple series, there are however some interesting numerical relations:

I.

	λ	√	Remarks.
1.	2907.4	34,394.97	A new line
	4150.6	24,092.90	A new line
		10,302.07	Frequency difference
2.	3082.3	32,443.3	(2, *p*)–(3, *d*) an arc line
	4513.0	22,158.2	An enhanced line
		10,285.1	Frequency difference

Although the frequency differences between these two pairs are almost equal, it is difficult to see why the arc line λ 3082, which belongs to the first subordinate series, should be linked with the enhanced line λ 4513.

II.

1. The frequency of the line at 4150.6 is closely represented by the equation

$$v = (2, p_2, \pi_2) - B(1) - (3, p_2, \pi_2),$$
$$v = 24{,}066.32 \text{ calculated,}$$
$$v = 24{,}092.9 \text{ observed.}$$

[1] Astrophysical Journal, 52, p. 47, 1920.

2. The frequency of the line at 2907.4 is fairly well represented by the equation

$$v = (2, p_2, \pi_2) - B(1) - (5, p_2, \pi_2),$$
$$v = 34{,}451.4 \text{ calculated},$$
$$v = 34{,}395.99 \text{ observed}.$$

The above symbols have the following values as given in Seriengesetze der Linienspektra by Dr. B. Dunz.

$$(2, p_2, \pi_2) = 48{,}279.51,$$
$$B(1) = 8{,}882.19,$$
$$(3, p_2, \pi_2) = 15{,}331.00,$$
$$(5, p_2, \pi_2) = 4{,}945.96.$$

While the agreement between calculated and observed values is not as close as might be desired the similarity in meaning of the two equations is suggestive.

University of Chicago.

The Aspherical Nucleus Theory Applied to the Principal Series of Helium.

By Ludwik Silberstein.

The quantum theory of spectrum emission combined with the assumption of a non-spherical, axially symmetrical nucleus, is applied to Fowler's principal series of helium, corresponding to the fixed total quantum number $n' = 3$ and the variable ones $n = 4$, 5, etc. The theoretical 'main' components, *i.e.*, those corresponding to the passage of the electron from a circular-equatorial to a circular-equatorial orbit, are correlated with the strongest components observed by Paschen in the first five groups or members of the series and with the centres of the next two members observed (but not split) originally by Fowler. The two constants appearing in the general formula, the modified Rydberg constant N and the coëfficient of asphericity σ are thus determined. The differences between the calculated and the observed wave-lengths are all within the error limits. The finally adopted values are $\sigma = 9.334 \cdot 10^{-4}$ and $N = 109723.22$. The latter, combined with a previously obtained value of N for hydrogen, gives for the ratio of the mass of the hydrogen atom to that of the electron the value 1817. The fine-structure depending on σ, through the product $N\sigma$, is then investigated and discussed numerically in the case of the first two members of the series, the groups 4686 and 3203. The distribution of the theoretical components shows, especially in the case of the first group, some similarity to Paschen's observations, although there are superabundant theoretical components.

Eastman Kodak Company.

A Physical Explanation of the Action of the New Singing Tube.

By Chas. T. Knipp and Jakob Kunz.

In the organ pipe energy is supplied by a stream of air which encourages the vibrations in a one-sided way, so that the vibrating column receives an impulse each time when the air moves upward towards the node in the middle of the pipe, and receives no impulse in the opposite motion. It looks as if a pendulum were kept in oscillation by receiving at one end of its path an impulse always in the same direction. If we would apply the momentum of the air jet at the center of the tube, vibrations of the column would be discouraged.

We can communicate momentum to a vertical open-air column by heating it. If we heat the air in a tube by a wire net placed in the lower half of the tube, we will obtain a uniform current of air upwards. If the air is vibrating then as it is moving inward its vibration is increased by the momentum of the upward stream of air, but not increased by moving downward. When we place the hot wire net in the middle of the tube it will tend to increase the pressure of the gas when it is a minimum, *i.e.*, it will discourage oscillations. The same will happen when we place the hot net above the middle. In order to encourage oscillations we have to add momentum in a position and at a moment such that the pressure in the node increases more than it would do because of the oscillations alone. If we put the hot wire net at the lower end of the tube, *i.e.*, in a loop, the effect will be very small or zero. The transfer of heat will depend upon the temperature of the air in contact with the wire net, being greatest when the temperature is lowest. But the temperature in the loop at the lower end does not vary, therefore, the transfer of heat in this position of the gauze does not give rise to oscillations. It tends only to raise the temperature of the gas uniformly. *Heat must therefore be applied between a loop and a node.*

If we cover the upper end of the tube, with the hot net in the most favorable position, the sound ceases, and if we heat by means of a Bunsen burner the outside at the top, we get no sound. This was considered by Rayleigh[1] as possible. But if we change the cross section of the tube at its middle, making the upper, closed part of larger diameter, then the tube will emit a sound. The pressure in the upper half of the tube will increase, partly because the air is heated, partly because of the condensations of the air in the node on the top. The air will expand and now the expansion in the narrow neck is aided by the air being heated by the wall. Here the oscillations are encouraged because each time when the air is expanding by the oscillation the expansion is increased by the heat. In each cycle the vibrating particle receives one push in the right direction. It is this one-sidedness of the action which encourages the oscillations. Moreover, as the heat here has the tendency to increase the pressure near the node, the oscillations will start very readily. A slight modification of this experiment is the glass blower's bulb with a long open

[1] Theory of Sound, Vol. II., p. 231.

neck below, which emits a sound when heated round about the neck. Instead of making the lower part of the tube narrower, we might have an annular area take the place of the narrow tube. Various other modifications are considered. In all cases, in the organ pipe, in Rijke's experiment (the second case) and in the other tubes, the oscillations of a column of air are maintained by a one-sided addition of momentum at the right moment and in the right place.

These experiments belong to a large variety of phenomena in which a direct motion is transformed into a periodic motion, electrically speaking, where direct current is transformed into an alternating current.

University of Illinois,
November, 1921.

Theory of Acoustic Wave Filters: The Limiting Frequencies of Transmission.

By G. W. Stewart.

In a former abstract[1] the writer presented the description of an acoustic wave filter and an approximate formula for its cut-off frequency. The theory has been slightly modified and has been extended to include three types of filters.

Definitions.—Using complex notation, *acoustic impedance* is the complex ratio of the pressure difference applied and the rate of change of volume displacement.

If X is the volume displacement, P the difference of pressure applied in a portion of the line, the definitions of the inertance, M, and the capacitance, C, are as follows:

$$\frac{Md^2X}{dt^2} = Pe^{i\omega t}, \qquad \frac{X}{C} = Pe^{i\omega t}.$$

Assumptions.—The chief assumptions are as follows:

Any portion of the system consists of mass and stiffness and hence the volume displacement with a sinusoidal applied difference of pressure can always be expressed by $Ie^{i\omega t}$, wherein I is complex.

The algebraic sum of the volume displacements at any junction is zero.

In the practical construction a short line is equivalent to an inertance and capacitance connected in parallel.

Results.—At least three filters are practicable, the single-band-pass filter, the low-frequency-pass filter and the high-frequency-pass filter. The following are the limiting frequencies of zero attenuation, for all three types:

$$f_1 = \frac{1}{2\pi}\sqrt{\frac{1}{M_2C_2}}, \qquad f = \frac{1}{2\pi}\sqrt{\frac{M_1 + 4M_2}{M_1M_2(4C_1 + C_2)}}.$$

All of these filters have been constructed and found to test out in remarkable agreement with the approximate theory.

State University of Iowa.

[1] Phys. Rev., March, 1921, p. 382.

DIFFRACTION EFFECTS IN SOUND ABSORPTION MEASUREMENTS.

BY PAUL E. SABINE.

THE familiar equation for the decrease of sound in a room with reflecting walls is

$$At = \log_e I.$$

A is the rate of decay, t is the time required for the sound to decrease to minimum audible intensity, and I is the initial intensity in terms of this minimum. The value of A is given by the equation

$$A = \frac{\Sigma a_1 s_1}{s} \cdot \frac{v}{p}.$$

The term $\Sigma a_1 s_1$ has been called the total absorbing power of the room and its contents and is the summation of the products of the areas exposed to the sound by the respective coefficients of absorption. v is the velocity of sound and p is the mean free path between reflections. The absorption coefficients of different materials have been measured by noting the difference in the duration of audible sound from known sources produced by bringing measured areas of these materials into a room whose absorbing power is known.

Recent experiments, under the improved conditions afforded by the Sound Chamber of the Wallace Clement Sabine Laboratory, have shown that the apparent absorbing power per unit area of highly absorbent materials is a function of the area of the sample tested, of its shape, and also of its location relative to other absorbing surfaces, when the dimensions of the sample tested are not great compared with the wave length of the sound. Measurements were made for tones one octave apart from C_2 (128 d.v.) to C_7 (4096 d.v.) with samples ranging from .14 to 10.0 square meters. For the frequency at which the absorption of felt is a maximum, namely 1024 d.v., the absorbing power per unit area decreased with increasing area, the ratio in the extreme cases being approximate 3 to 1. The same effect was observed at other frequencies although the variation was not so great.

Long narrow shapes with an area of 3.3 square meters showed an absorbing power some 50 per cent. greater than an equal area in the form of a square.

By a similar method the passage of sound through rectangular openings, varying in size from .34 to 2.8 square meters and having a constant ratio of dimensions, was measured. The same effect was observed as in the case of absorption by the felt. For example, the relative transmissions of C_4 (512), per unit area through the smallest and the largest openings were in the ratio 11 to 8.

A considerable number of experiments have been made, all of which suggest the phenomenon of diffraction in the passage of sound through small openings, and obviously suggest some qualifications in the definition of sound absorption coefficients.

WALLACE CLEMENT SABINE LABORATORY,
RIVERBANK, GENEVA, ILLINOIS.

Analysis of the Energy Distribution in Speech.

By I. B. Crandall and Donald MacKenzie.

An analysis is made of the energy distribution in average speech, with the assumption that the energy is continuously distributed over a wide frequency range. The speech is received by an electrostatic transmitter whose voltage output, amplified about 3,000 fold, is impressed on the grids of twin single-stage amplifiers. The unmodified output of one of these amplifiers is measured by a thermocouple and is a known function of the total energy received by the transmitter. The output of the other amplifier is limited by a series resonant circuit to a narrow band of frequencies, the energy in this band being measured by a second thermocouple.

The entire range from 75 to 5,000 cycles per second is covered by twenty-three settings of the resonant circuit. It is found that at frequencies higher than 5,000 cycles the energy is so small as to be incapable of measurement with this apparatus.

The procedure followed in the observations is to utter, syllable by syllable, a 50-syllable piece of discourse, maintaining as nearly as possible the normal modulation of the voice as when speaking without interruption. As each syllable is spoken readings are made of thermocouple currents (the couples here function as ballistic galvanometers) for both total output and resonant circuit transmission. Such a series of readings is made at each setting of the resonant circuit. Corrections are applied to the results to take into account the transmitter-amplifier characteristic, the transmission characteristics of the resonant circuit, and the unavoidable variations in total energy incidental to frequent repetition of a given syllable.

Curves are obtained for individual voices (4 male, 2 female) and from these a composite curve is drawn. This curve shows a great concentration of speech energy in the low frequencies, a result which would not be expected from previously published data of other experimenters. In view of the fact that with the present apparatus a practically uniform accuracy is attained throughout the whole frequency range it is believed that the results obtained are indicative of the actual energy distribution.

Research Laboratory of the
American Telephone and Telegraph Company
and Western Electric Company, Inc.

The Separation of the Element Chlorine into Isotopes (Isotopic Atomic Species).

By William D. Harkins and Anson Hayes.

A definite increase in the atomic weight of chlorine, equal to 1.55 parts in one thousand, was obtained by Harkins and Broeker in January, 1920. This seems to be the first separation of isotopes reported for which there is any

definite evidence. In the present investigation an altogether independent separation has been carried out on a larger amount of material, and a number of atomic weight determinations have been made with extreme care upon very carefully purified material. These prove that the separation is an actual one and not due to impurities. In all there have been obtained about 4 grams of chlorine of atomic weight 35.515, ten grams of atomic weight 35.498, and 90 g. of atomic weight 35.494, on the basis of a normal atomic weight of 35.460. In addition to this many kilograms of material of both higher and lower atomic weight than the normal have been collected, but the atomic weights of these samples have not been determined. The experiments thus far have been carried out by the diffusion of hydrogen chloride at atmospheric pressure, but the later diffusions will be conducted at low pressures.

The following table gives the increase in atomic weight which should be obtained by diffusion provided the Rayleigh theory holds. The cut gives the number of grams of the substance which must be taken in order to give one gram of product provided the process has an efficiency of 100%.

Cut.	Increase of Atomic Weight.	
	HCl.	Neon.
10	0.021	0.020
100	0.044	0.042
1000	0.067	0.065
10000	0.091	0.091
100000	0.116	0.120
1000000	0.142	0.151
10000000	0.169	0.182

It will be seen that the increase in atomic weight is very nearly a constant times the logarithm of the cut.

UNIVERSITY OF CHICAGO.

ON THE DETERMINATION OF SURFACE THERMAL CONDUCTIVITIES.

BY LETHA A. SMITH.

IT is well known that when heat is transferred through a gas between vertical plane solid boundaries the circuit can be considered to consist of the plates, the this regions of relatively stagnant gas at the surfaces of the plates, and the main body of the gas between these partially stagnant portions. In considering the total equivalent conductivity of this, and of many other arrangements, we find that these partially stagnant surface regions frequently play the most prominent part.

The apparatus which is being used for the study of the equivalent conductivity of these regions consists primarily of six parallel plates of glass or metal, which are separated by insulating frames of wood and rubber. These are

clamped together and give a convenient water-tight apparatus. Each of the five compartments can be continually supplied with water or air by means of tubes let into the frames; and opening are provided for inserting thermometers, thermocouples and stirrers.

The central compartment is filled with hot water, the two outer compartments with flowing cold water at a constant temperature, and the two intermediate compartments with air, these air spaces being the ones across which the conductivity is to be measured. The rate of cooling of the central compartment (and under converse conditions, the rate of warming) is found to give curves of an exponential character, showing that Newton's law of cooling holds over the temperature range investigated. In an apparatus designed in this way, the customary difficulties of a thermal investigation are to a large extent eliminated, and allowances for the comparatively small influence of external conditions can easily be made.

It may be shown that it is possible to calculate the equivalent conductivity of these relatively stagnant regions at the surfaces of the solid boundaries by an analysis (1) of a cooling experiment similar to the one mentioned above, (2) a cooling experiment in which flowing cold water at a constant temperature replaces the air in the first experiment, and (3) a record of temperature gradients as determined by thermocouple measurements. The following values have been obtained for the conductivity of these regions: 33.4×10^{-2} calories per square centimeter per minute per degree Centigrade when the boundary is window glass; and 2.92×10^{-2} to 1.97×10^{-2} calories when the boundary is brass. The latter values depend on the condition of the surface.

McGill University.

The Causes of Reaction Expansions in Amalgams.

By Arthur W. Gray.

This communication offers a simple theory to account for the hitherto unexplained peculiar alternation of contractions and expansions that a dental amalgam undergoes during and after the process of hardening.

The rapid drop to a minimum that forms the first part of the typical curve of reaction expansion evidently represents the end of the stage in which there is predominance of the contraction accompanying solution of the alloy in the mercury and formation of Ag_3Hg_4.

Crystallization of the Ag_3Hg_4 quickly follows its formation. The first minimum in the curve marks the time when the rapidity of the expansion accompanying this crystallization just equals the rapidity of the contraction caused by the simultaneous formation of more Ag_3Hg_4.

As the solution and reaction diminish, the crystallization expansion comes to predominate. This predominance is indicated by the rise of the curve from the first minimum to the first maximum.

The mixing of the alloy with the mercury, whether by trituration or other-

wise, reduces the alloy to particles of microscopic size. Many, if not most, of these particles must, however, be considerably larger than molecules at the time the amalgam is molded into a test specimen.

Consequently, there will be a gradual inward diffusion of the free mercury coating the alloy particles, resulting in still more solution, reaction, and crystallization, which may continue long after the amalgam has begun to harden. The volume changes resulting from this diffusion might easily account for the slow descent of the typical reaction expansion curve after reaching the first maximum, and the very much slower rise that follows.

The gradual changes in shape that the reaction expansion curve can be made to undergo by systematic variation of influencing conditions are exactly what might be reasonably expected if the foregoing hypothesis is correct. Illustrations of such changes are given elsewhere.[1]

CAULK PHYSICAL RESEARCH LABORATORY,
MILFORD, DELAWARE,
December 12, 1921.

THE POROUS PLUG COEFFICIENT FOR AIR.

BY J. R. ROEBUCK.

WORK has been in progress intermittently for some years in this laboratory on the Joule-Thompson effect. Papers have been published on a form of plug[2] and on work with water leading to the mechanical equivalent.[3] Sufficient progress in the problem with air has been made that the accumulation of thoroughly reliable data appears to be only a matter of considerable labor. The initial temperature is controlled by passing the air through a pipe immersed in a fluid which also surrounds the plug chamber, and whose temperature is controlled by an electrical resistance thermostat with coils of pure nickel wire or of manganin. The initial pressure is controlled by a rotating piston regulator whose excursions control a spill valve. The radial form of porous plug is used (l.c., 1). In the pressure range 45–200 atoms, the mass flow past the low pressure thermometer inside the plug can be made large without the kinetic energy of flow becoming appreciable. Data in this field can be duplicated readily with different plugs and different rates of flow. Curves have been obtained foi initial temperatures of 25, 50, 75, and 100° C. They are markedly curved, convex toward the temperature axis. Both slope and curvature fall off rapidly from low to high temperature, so that apparently the coefficient will go to zero at about the same temperature (225° by extrapolation) for the whole pressure range.

For the pressure range 1–45 atmospheres, the increased volume of the air

[1] A. W. Gray, Contractions and Expansions of Amalgams with Time, PHYS. REV., *18*, 108–113, 1921. Also, Metallographic Phenomena Observed in Amalgams, Am. Inst. Min. and Met. Eng. Trans., *60*, 678–697, 1919; Journ. National Dental Assn., *6*, 909–925, 1919.

[2] Burnett & Roebuck, Plugs, Rev., 30, 529, 1920.

[3] Physics Rev. (2), II, 79, 1913.

passing the low-pressure thermometer leads quickly to either a markedly increased coefficient which increase depends on the rate of flow and is therefore due to kinetic energy effects; or to such a small heat capacity passing the plug that the errors due to heat gain and which are determined largely by the difference of temperature, become larger than desirable. Warming curves of the plug with the flow stopped may be used to get the maximum value of these corrections. Data have been obtained with the low side pressure appoaching one atmosphere where the values of the coefficient were independent of rate of flow.

Great difficulty has been experienced in obtaining suitable porosity. The plugs used are made of porous porcelain and the porosity reduced to that desired by precipitating barium sulphate within the wall. Unfortunately the precipitate blows out. Repeated fillings lead to very non-uniform porosity and consequently erratic values for the coefficient.

Apparatus is at hand for covering the temperature range + 250° C. to about − 100° C., and the pressure range 1–200 atmospheres. It will be extended to other gases when the air data are completed.

University of Wisconsin,
December 10, 1921.

Ether-drift Experiments at Mount Wilson Solar Observatory.

By Dayton C. Miller.

The ether-drift interferometer with a light-path of 224 feet, which was used by Morley and Miller in the Cleveland experiments of 1904 and 1905,[1] has been remounted at the Mount Wilson Observatory in southern California, and observations were obtained in April and in December, 1921. In some of the earlier observations made on a slightly elevated location there was a small displacement of the interference fringes such as would be expected from a true ether-drift. The present series of observations had the object of determining whether this displacement would be larger at the elevation of about 5,900 feet above sea level, and whether it would be affected by the change in the direction of the earth's motion in space from April to November. It was further decided to determine whether the effect was due to magnetic disturbances, by using a steel base for the optical parts in April, and a concrete base in December.

The results show a definite displacement, periodic in each half revolution of the interferometer, of the kind to be expected, but having an amplitude of one tenth of the presumed amount. This is slightly larger than the displacement obtained in Cleveland in 1905. However, this displacement is always accompanied by a disturbance, periodic in one complete revolution of the interferometer, the cause of which is so far unexplained. Final conclusions cannot be drawn until this disturbing factor has been eliminated, by further

[1] Philosophical Magazine, May, 1905.

experimentation. The observations show that the effect is not due to magnetism, and that its magnitude is about the same in April and December.

CASE SCHOOL OF APPLIED SCIENCE,
CLEVELAND, OHIO,
December 20, 1921.

PHOTO-ELASTICITY OR OPTICAL INVESTIGATION OF STRESS DISTRIBUTION IN SOLID BODIES.

BY PAUL HEYMANS.

THE object of the mathematical theory of elasticity is the analytical determination of the elements defining the elastic state at any point of a solid body, *i.e.*, the directions and the algebraic values of the principal stresses.

The number of cases for which a complete mathematical solution exists is limited and the calculations usually worked out in practice for the computation of stability are in general an adaptation, with simplifying assumptions of sometimes doubtful accuracy, of the ideal and incomplete theoretical solution to the needs of engineering practice.

The photo-elastic methods,[1] lead to the experimental determination of the stress distribution for all two-dimensional elastic problems, provided the material in use is isotropic and obeys Hooke's law of linear proportionality between strain and stress.

Those methods are based upon the temporary birefracting properties shown by transparent bodies, namely by xylonite, when put under stress. By means of: (1) *plane polarized light*, the isoclinic lines from which the lines of principal stress, *i.e.*, *the directions*, (2) *circular polarized light, the values of the difference*, (3) *a lateral extensometer, the values of the sum of the principal stresses are determined* at each point of the body under examination.

As in the two-dimensional elastic problems the stress distribution is independent of the elastic constants, *i.e.*, of the nature of the substance, the stress distribution within the elastic limit is the same for any isotropic substance, xylonite, steel, or others, obeying Hooke's law.

Those methods become of valuable help for the development of general mathematical solutions of elastic problems and also for the direct investigation of specific engineering problems. It is desirable that they be extended to the three-dimensional problems.

The theoretical development of photo-elasticity is in the field of physics; their application chiefly interests the engineer. The author therefore brought their description before the Am. Phys. Soc. and in an address to the Eng. Section of the A. A. A. S. he afterwards considered the application of photo-elasticity to engineering problems.

[1] The development of the photo-elastic methods is largely due to Dr. E. G. Coker, Univ. of London, with whom the author of the paper collaborated in recent research in that line.

Experiments on the Sign of the Electric Charge Assumed by a Metal Immersed in a Liquid.

By Richard D. Kleeman and William Fredrickson.

A knowledge of the sign of the electric charge assumed by a metal plate immersed in a liquid or solution is of importance in the theory of the e.m.f. of a cell and in connection with other subjects. Information about this point may be obtained from the motion of metal particles in colloidal solution under the influence of an electric field. But this method suffers from the disadvantage that the process of getting the particles into colloidal solution may change, and in most cases does change, the surface of the metal particles through the formation of oxides, hydroxides, etc., which might have the effect of changing the sign of the electric charge on the particles. The information obtained from difference of potential and electro-capillary measurements, in the cases where they can be applied, is rendered somewhat untrustworthy on account of the hypotheses underlying the interpretation of the experimental results. A set of experiments was accordingly undertaken which should give trustworthy results, and in which it was made certain that the metal surfaces initially were clean.

Fine wires of different metals were in succession suspended in a liquid by means of a fiber about two meters long, a current sent through the liquid, and the direction of the deflection of the wire noted through a microscope. The wires were carefully cleaned by means of fine sandpaper before being used. In this manner it was found that the metals Cu, W, Ag, Mo, Mg, Al, C, Ni, Au, Pt, Sn, Zn, immersed in distilled water assume a negative charge, or move in the opposite direction the current is flowing, while the metals Bi, Pb, Fe, Cd, assume a positive charge. The metals Bi, Pb, Fe, Au, Pt, Ag, have been obtained in colloidal solution in water and their motion under an electric field measured, which indicates that the metals Au, Pt, Ag, are negatively and the metals Bi, Pb, Fe, positively charged. This falls into line with the preceding results, and in the case of these metals at least the process of getting them into colloidal solution does not affect the sign of their ultimate electric charges.

Union College,
Schenectady, N. Y.

The Analysis of Simple Periodic Curves by a Projection Method with Special References to Estuary Tidal Problems.

By E. V. Henry.

A simple method of projection analysis has been developed which can be applied with great advantage over the customary harmonic analysis to certain special types of periodic curves. It has been used particularly in the case of tidal records for large estuaries such as the river and gulf of St. Lawrence. In the case of estuary tidal analysis by the harmonic methods the Fourier

constants are numerous and arbitrary in character, and they neither correspond individually to separate physical factors nor do they even lead to the expression of any satisfactory empirical relationship between any one tide and any other tide on the same estuary. This makes the analysis for estuary tides fundamentally different from that of ordinary tides where the Fourier constants have a direct physical interpretation with reference to solar and lunar movements.

The apparatus consists of three concentric frames which may be turned in such a manner that an attached graph may be inclined into any plane and the defining angles noted. A beam of light from a suitable illuminating source with a specially chosen lens enables one to obtain a normal parallel beam for projection. A glass plate for recording the projected graph is placed at right angles to the beam.

The theory of the apparatus may be developed from the elements of analytical solid geometry.

The results obtained in the case of estuary tides appear to be most interesting.

1. Any tidal graph for any one of the tidal stations on the St. Lawrence estuary could be projected into any other which was further up the river. Similar projections were possible also in the case of each of the estuaries examined, for example that of Port Essington into that of Port Simpson, in British Columbia; and that of Carter's Beacon into that of Root Creek, in Hudson Bay. In each case only three constants were used. Professor Dayton Miller very kindly arranged to have some of these graphs analyzed by the harmonic method in his laboratory at Cleveland, and it was seen that as many as ten constants were used which varied from tide to tide.

2. It appears probable that a method of prediction for estuary tides, which is sought by hydrographers, may be based on the above relationships. In order to test this the tidal curve at Levis was projected into the curve obtained at Platon, using only two angles. One of these remained the same throughout, whilst the other varied from tide to tide. A graph was plotted with the number of the tide as abscissa and the changing angle as ordinate, the result was a curve which repeated itself every fifty-six tides, and could over a limited range be used for purposes of prediction.

The writer is greatly indebted to Dr. Bell Dawson and to Dr. A. N. Shaw for their keen interest, for the assistance rendered by furnishing the tidal data and for numerous suggestions.

McGill University.

A Galvanometer Method for Producing at a Distance a Magnified Record of a Mechanical Motion.

By F. Wenner.

The purpose of the investigation is the development of a method for producing at a distance a magnified and fairly accurate record of irregular relative

displacements of two elements of a mechanical system. Examples of motions to be recorded are the relative displacement of a horizontal pendulum and its support caused by earthquakes, and the relative displacements of two points on a bridge member caused by transient loads. The method consists essentially in the use of,

(*a*) A coil of insulated wire and a magnet attached respectively to the two parts whose relative motion is to be recorded.

(*b*) A moving coil galvanometer.

(*c*) An inductance connected in parallel with the galvanometer.

(*d*) A pair of insulated conductors or line connecting the coil, whose motion relative to the magnet is to be recorded, and galvanometer.

(*e*) An optical system including the mirror of the galvanometer and a moving photographic film.

The coil and magnet attached to the two parts of the mechanical system whose relative motion is to be recorded are located in what we shall refer to as the originating station. The rest of the apparatus, excepting the line, is located in what we shall refer to as the recording station. The line connects the originating and recording stations.

A relative motion between the coil and magnet in the originating station develops an electromotive force which causes a current in the circuit. This current divides between the inductance and the galvanometer, and that part which passes through the galvanometer causes a torque tending to displace the coil from its equilibrium position.

The optical system produces an image of a line source of light on the moving film and, as it includes the mirror of the galvanometer, gives a record of the motion of the coil of the galvanometer.

With this arrangement the galvanometer has an extra period of vibration which is short in comparison to the period determined by the moment of inertia of the coil and the torsional constant of the suspensions. The vibration in this extra period may be either over damped, critically damped, or under damped, depending upon the relative magnitude of the quantities involved. The conditions giving critical damping and a period of about one tenth of a second may be realized with galvonometers such as have been on the market for a number of years and which have free periods from five to fifteen seconds. By designing the galvanometer especially for this purpose, critical damping with a considerably shorter period should be possible. An important feature of the method is that the sensitivity to those components in the motion to be recorded corresponding in period to the extra period of the galvanometer is only slightly greater than for those components having half this period or several times this period.

The magnification obtainable will depend upon the size of the magnet and the coil used in the originating station, the nature of the apparatus to which the magnet and coil may be attached, the highest frequency component of the motion to be recorded, the accuracy of the record desired, and the resistance

of the line connecting the originating and recording stations. In general, however, the magnification may be as large as desired.

The distance permissible between the originating and recording stations depends to a very large extent upon the same quantities as the magnification. In most cases, however, the distance may be as large as desired up to fifty miles or even more, except in case a high magnification is also desired.

In case of an irregular motion the highest frequency components which may be considered as recorded will depend to a considerable extent upon the accuracy required and pains taken in the design and construction of the apparatus. It should, however, be possible to get a fairly definite idea of the amplitude of the components having frequencies up to fifty cycles per second.

When the coil of the galvanometer is deflected the suspensions exert a torque towards a definite equilibrium position. For this reason very slow motions are not recorded, and this will be a decided advantage in the case of seismometers which are very sensitive to changes in level.

The conclusions stated above were reached mainly from observations of the action of apparatus set up for demonstration purposes, and from calculations made for a single special case. This should therefore be considered as a preliminary report upon the work.

DEPARTMENT OF COMMERCE,
BUREAU OF STANDARDS,
WASHINGTON, D. C.

THE INFLUENCE OF SMALL VARIATIONS IN THE OUTLET OF A SMOOTH BRASS TUBE ON THE DISTRIBUTION OF STATIC PRESSURE WHEN AIR IS FLOWING THROUGH THE TUBE.

BY T. S. TAYLOR.

WHILE measuring the flow of air through a smooth brass tube 150″ long and 7/8″ diameter, it was observed that peculiar variations of the static pressure existed at the outlet. The static pressure for this tube was found to be less than atmospheric at the outlet and it was necessary to move the measuring tube several centimeters back into the brass tube at the center before the static pressure had become atmospheric. As far as could be observed mechanically the tube was smooth, both as to the way it was cut off and as to the existence of bevels or burrs. Results were obtained for different velocities of air, of the distribution of the static pressure for various positions near the outlet and a set of curves obtained, showing the distributions across the tube as well as along the tube. Further microscopic examination of the end of the tube finally revealed an extremely small bevel which was the cause of the disturbances observed. This was undoubtedly there since after taking extreme pains to have the end of the tube smooth and cut off squarely, the static pressure was always atmospheric at the outlet and the distribution was constant across the tube.

A further study was then made to get some ideas relative to the influence of different bevels upon the changes in the static pressure at the outlet. The static pressures were always measured by a carefully constructed static pressure tube made from a small hypodermic needle. A sensitive inclined gage was used to measure the static pressures.

Westinghouse Research Laboratory.

Cohesion and Adhesion.

By Wilson Taylor.

From evidence presented in the Philosophical Magazine, June, 1921, pp. 877–889, on "The Coalescence of Liquid Spheres," it is inferred that the force of surface tension is a fundamental property of all free surfaces of mass, acting about the free molecular masses of a gas and causing the molecules to coalesce or cohere in the same way as liquid spheres are observed to do.

Accordingly, measurements were made on mercury spheres suspended freely from the lowest rims of water drops. These spheres ranged in size from .006 mm. to 1.5 mm. in diameter. The vertical lift upon the mercury of the surface tension of the water was compared with the weight of the suspended sphere and it was found that the upward lift was always greater than the weight except when the spheres, on account of their size, were on the point of falling off, and then these two forces were equal. For the smallest sphere the upward lift was seven times the weight.

Again, similar measurements were made on mercury spheres suspended from glass surfaces and ranging from .002 mm. to 2.25 mm. in diameter; and, as before, the vertical lift of the surface tension of the mercury at the line of its attachment to the glass was compared with the weight of the suspended sphere. It was found that the vertical lift as the spheres increased in size gradually decreased from about 13,000 to 2.29 times the weight. Had the surface tension of glass having a value of 239 dynes per cm. been used instead of that of mercury this ratio would have decreased from 6,000 to one of equality as the spheres were on the point of falling off.

Similar evidence in the case of solid bodies suspended from water and of small solid bodies adhering to each other with or without a liquid connecting link showed that as far as could be observed microscopically the same law was in operation.

Also from the evidence referred to above there is reason to think that the law operates as well in the case of molecular masses, that is,

Cohesion and adhesion are simply surface tension forces which exist about all free masses, molecular or larger, attaching themselves to each other in the periphery of the contact area and binding the two masses together in one enveloping surface tension force.

There is thus no evidence of any molecular attraction between the two

masses in the contact area itself but an actual pressure of the one mass upon the other reaching in the case of a water molecule to about 11,000 atmospheres.

UNIVERSITY OF TORONTO,
December 30, 1921.

PROGRESS OF WORK WITH THE CRYSTELLIPTOMETER ON SELENIUM CRYSTALS.

BY LEROY D. WELD.

A CONTINUATION of work treated in a previous paper.[1] The results indicate that fairly consistent data on optical constants can be obtained by reflection even from old crystals of selenium unless accidentally contaminated. There is strong indication of anomalous dispersion, suggesting an absorption band, in the vicinity of wave-length 0.6 micron. Paper will be published immediately in the Journal of the Optical Society.

STATE UNIVERSITY OF IOWA.

THE TRANSMITTED EFFECT IN SELENIUM CRYSTALS.

BY J. C. POMEROY.

LONG needlelike crystals were used, each of which was clamped by electrodes at one or more points.

Measurements were made of the transverse conductivity in the dark and also of the change in this conductivity when a narrow band of light was allowed to fall at the electrodes and at points along the crystal spaced 0.5 mm. apart.

This change of conductivity and its logarithm were plotted against the distance between the electrodes and the spot of light. In general this logarithm was proportional to the distance. In some cases there were marked variations from this rule but these generally could be traced to certain peculiarities in the formation of the crystal.

From the observed facts the writer is led to think that the light effect is transmitted along the crystal by some sort of wave motion. It is hoped that experiments now in progress will throw some further light on this theory.

BETHANY COLLEGE,
WEST VIRGINIA.

FURTHER EXPERIMENTS ON CRITICAL POTENTIALS IN HYDROGEN.

BY F. L. MOHLER, PAUL D. FOOTE, AND E. H. KURTH.

THE discrepancies between previous results of various observers as to the values of critical potentials of hydrogen as well as the differences in interpretations of results led to the following experiments.

A four-electrode tube was constructed with a photo-electric source of electrons instead of the usual thermionic cathode. The arrangement of electrodes

[1] Abstract, N.S., Vol. 11, p. 249, 1918.

and methods of measurement were similar to those used before by two of the authors.[1]

A potassium hydride surface illuminated by an incandescent lamp gave currents ample for measurement of the principle ionization potential and potentials of inelastic impact. Consistent initial potential corrections were obtained from measurement of the potential at which the total current started. The ionization potential thus corrected was 16.0 volts. Inelastic collisions occurred at 10.5 and 22.3 volts.

The photo-electric cathode was replaced by a Wehnelt cathode. The results obtained were practically identical with the above at the same pressures. With higher pressures inelastic impacts occurred at 10.5, 16 and 21 volts. In this respect the results are entirely consistent with the work of Mohler and Foote.

As the above method of applying initial corrections may be questionable, measurements were made with mercury vapor as well as hydrogen in the tube. Pressures were adjusted to give nearly equal amounts of ionization from the two gases and the difference between ionization points was measured. The resulting value for hydrogen is 15.5 volts.

We conclude from the above results that the dissociation of hydrogen by an incandescent wire plays no appreciable part in the phenomena observed. The potentials of inelastic collision at 10.5 and 22.3 indicate resonance potentials at 10.5 and 11.8 volts, due to collisions with normal hydrogen. The possibility that 22.3 volts is a resonance potential and not due to successive impacts is not excluded by this work.

Bureau of Standards.

Photo-electric Phenomena in Coated-filament Audion Bulbs.

By R. C. Gibbs and Edna L. Meacham.

Case[2] and Merritt[3] have recorded certain observations made upon the photoactive behavior of coated-filament vacuum tubes. Additional experiments intended to examine in more detail some phases of their work have been performed.

With one of the tubes previously used by Merritt, study was mainly made upon the increase in thermionic current that occurs when the coated filament is illuminated. This increase will be referred to as the photo-electric current. For various voltages applied between filament and plate the photo-electric current was found to increase with increase of filament current in very much the same way as the thermionic current. The size of the photo-electric current depended upon the potential of the grid. In order to eliminate a steady drift in thermionic current which was in one direction when the grid was connected to the plate and in the opposite direction when the grid was

[1] Bureau of Standards, Sci. Paper No. 406.

[2] Phys. Rev., Vol. XVII., p. 398, 1921.

[3] Phys. Rev., Vol. XVII., p. 525, 1921.

connected to the filament, a high resistance was connected between filament and plate and the grid connected so as to maintain it at a potential between that of filament and plate. With this connection the photo-electric current reached values as large as 24×10^{-8} amperes for a filament current of 0.9 ampere when it was illuminated by a 400-watt incandescent lamp operated on a storage battery and placed about one foot from the filament of the tube, a narrow slit being interposed to prevent illumination of other parts of the tube. With the grid floating a maximum for the photo-electric current was found for various plate potentials at a filament temperature corresponding to a filament current of about 0.83 ampere. For constant filament current the photo-electric current showed a saturation effect at the higher plate potentials.

It was found that from 8 to 10 minutes were required for the photo-electric current to reach its maximum after turning the illumination on the filament. Furthermore the decay of this current after the illumination was turned off was rather slow. The time of decay varied from 25 to 50 minutes depending upon various conditions of plate potential, filament current, and previous treatment of filament.

The ratio of photo-electric current to thermionic current for the same filament temperature decreased with increase in filament current, with an irregularity that often showed a distinct minimum and maximum between 0.5 and 0.6 ampere in the filament. This irregularity may be due to the fact that the filament was not brought to the same initial condition before the determination of each ratio.

It was early discovered that the ratio just mentioned depended, for a given filament temperature, to a very great extent upon the temperature and light treatment of the filament just previous to its determination.

A long series of observations were made at one filament temperature to determine the effect of this previous temperature and light treatment. At the filament temperature used, that corresponding to a filament current of 0.5 ampere, the ratio of photo-electric current to thermionic current was much larger when the filament had been illuminated at a higher temperature for some time just before. Previous illumination at a lower temperature reduced the ratio. If the filament were not illuminated during these higher and lower temperature treatments the ratio in each case was larger than when illuminated, the difference being more marked for the lower temperature treatment.

CORNELL UNIVERSITY,
August, 1921.

THE INFORMATION SERVICE OF THE NATIONAL RESEARCH COUNCIL.

BY ROBERT M. YERKES.
Chairman, Research Information Service.

THE *clearing-house* for science and technology, established by the National Research Council in 1919, has developed rapidly. It now contains uniquely valuable informational apparatus whose serviceability to investigators will increase as it is perfected and utilized in answering requests.

The Service has specialized on the varieties of informational need which are suggested by the questions who, what, where, and how. Who, refers to the persons engaged in research or qualified for it by training—there are more than 13,000 included in the Personnel File. What, refers to current research, distribution of research interest and activity, problems, published reports of results, bibliographies, bibliographic lists, abstracts, etc. Where, relates to research laboratories and institutes—their construction, equipment, resources and activities. How, concerns methods, processes, technique, apparatus and supplies for research and teaching.

Physicists are urged to acquaint themselves with the organization and functions of the Research Information Service and to avail themselves of its aid. In a multitude of ways it can be made to conserve their time, facilitate and improve their teaching and research. The more the Service is used by those who are actively engaged in the physical, mathematical and biological sciences and their respective branches of engineering, the more valuable it will become.

National Research Council,
Washington, D. C.

Power Factors in Radio Circuits.

By N. H. Williams.

A circuit containing inductance and capacity in series, when used in continuous wave work, is seldom permitted to oscillate at its natural frequency because it is invariably coupled to some other circuit. Hence its power factor may differ widely from unity and the behavior of the system is largely determined by the power factor.

This paper presents a method of measuring the phase relations of two high frequency currents which involves the measurement of each of the two currents, their vector sum, and their vector difference. Two wire loops, each about 20 cm. in diameter, are placed in series and connected to a short constantine ribbon used as a heating element. This element is placed near to a thermal junction and the other junction of this circuit is placed near to a second heating element which is supplied with current from a dry cell. A sensitive galvanometer is used in connection with the thermal junctions. The positions of the two heating elements are adjusted so that they produce equal and opposite effects upon the galvanometer when they both carry the same current.

An auxiliary coil of a few turns is connected into the high frequency circuit. This coil is placed parallel to one of the loops and about 10 cm. from it. There is induced in the loop a current which is proportional to the initial high frequency current. The current from the dry cell is now adjusted to balance the effect of the high frequency current upon the thermal junction and galvanometer and the value of the induced high frequency current is read from the D.-C. ammeter.

A second coil of the same size carrying current of the same frequency may now be placed near the second loop. When the battery current is adjusted to balance the combined effects of the two currents, the ammeter reads their vector sum. By constructing the vector diagram, the phase difference may be measured. The angle thus measured is the complement of the angle whose cosine is the power factor of the oscillatory circuit.

By this means the relations of power factor to frequency, to coupling, and to resistance have been investigated.

UNIVERSITY OF MICHIGAN.

"J" RADIATION: A SUMMARY.

BY F. K. RICHTMYER.

THE frequent reference in the literature of X-rays to the existence of a "J" radiation, of shorter wave-length than the K radiation, seems to warrant a statement summarizing the evidence pro and con, particularly in view of a recent paper by Crowther (Phil. Mag. for November, 1921 (10)).

Previous to that of Crowther, the evidence in favor of the "J" radiation has been based almost entirely on apparent discontinuities in absorption as a function of wave-length. The present writer has shown (8, 9) that, when absorption measurements are made with monochromatic radiation and with a precision of the order of one per cent., these discontinuities disappear.

Crowther bases his evidence for the existence of "J" radiation on the decrease in "hardness" of scattered radiation as compared with the primary beam transmitted at 45° through a thin sheet of aluminum, the scattered beam being measured at 90° from the primary. Since Crowther did not use monochromatic radiation his results (his published data are very meager) can readily be explained by assuming that the scattering coefficient is a function of wave-length.

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CORNELL UNIVERSITY,
December, 1921.

The Dilemma of the Helium Atom.

By John H. Van Vleck.

The study of helium, the simplest atom except hydrogen, should be a key to a generalized Bohr theory of atomic structure. However, no satisfactory model of normal helium has yet been devised, for the models of Bohr, Langmuir, Franck and Reiche, and Landé all give the wrong ionization potentials if the non-radiating orbits are determined by the Sommerfeld quantum conditions.

It therefore seemed desirable to compute the ionization potential of a model suggested by E. C. Kemble,[1] in which the two electrons, I. and II., move in three dimensions with an axial symmetry, so as to have the cylindrical coordinates

$$\text{I. } r, z, \varphi, \qquad \text{II. } r, z, \varphi + \pi.$$

After the dynamical solution was obtained as a power series in a parameter, the constants of integration were determined so as to give the action integral the value demanded by the Sommerfeld quantum conditions, assuming one of the coördinates to be used was the cyclic coördinate φ (giving the system a total angular momentum $h/2\pi$), while the other coördinates were unrestricted, provided they have the period of r and z. The computed ionization potential (74.9 volts) does not agree with the experimental value (79.3 volts), the discrepancy being of the same order as in the Bohr model, which gives an ionizing potential of 82.7 volts.

Since all the simple, symmetrical models of helium, such as are required by its extreme chemical stability, seem to yield impossible ionization potentials, some radical modification of the conventional quantum theory of atomic structure appears necessary. Two such possible modifications are:

1. Reformulation of the quantum conditions. Two very interesting such suggestions have been made by Langmuir.[2] One of these, that the maximum angular momentum of a single electron should equal $h/2\pi$, leads to a correct ionizing potential for his semi-circular dynamical model of helium, but appears contradictory to the fact that in the hydrogen atom and in the theory of rotational specific heats the total angular momentum of the entire system, rather than of a single electron, is $h/2\pi$. Also one would expect this modified quantum condition to be equally applicable to Langmuir's semi-circular hydrogen molecule, almost identical with his helium atom, but computations by the writer indicate that in this case the maximum angular momentum of an electron is not $h/2\pi$, but $.956(h/2\pi)$.

Langmuir's other suggestion, that of a static atom in which the electron is subjected, in addition to the Coulomb force, to a force which it would experience if it were an electrical doublet of strength $1/2em(nh/2\pi)^2$ does not appear to be consistent with the Rutherford scattering experiments, or with the dynamical orbits found in band spectrum theory. Also complicated modifications to the

[1] Phil. Mag., Vol. XLII., p. 132 (July, 1921).

[2] Physical Review, Vol. XVII., p. 349; Vol. XVIII., p. 104.

force would be necessary to account for the Sommerfeld fine-structure or even the shift between the lines of the Balmer hydrogen series and those of the Pickering helium series.

2. Modification of the law of force between negative electrons. The experimental evidence of Rutherford establishes the validity of the inverse square law only between negative electrons and positive nucleii, while Compton concludes that the spiral tracks of beta particles indicate that the field of an electron does not have a spherical symmetry.[1]

HARVARD UNIVERSITY.

MOMENT OF MOMENTUM OF MAGNETIC ELECTRONS.

BY E. H. KENNARD.

ACCORDING to the usual electron theory ferromagnetism is due to the circulation of electrons along paths of considerable length and must therefore be accompanied by mechanical angular momentum equal per unit volume to

$$\Gamma = k\frac{m}{e}I, \tag{1}$$

where I = intensity of magnetization, m/e = ratio of electronic mass and charge in electromagnetic units and k has the value 2. This equation is confirmed as to sign by E. Beck,[2] but he finds $k = 1$ for both iron and nickel. Barnett's results on magnetization by rotation likewise agree as to sign but indicate for k a value decidedly smaller than 2.

A smaller value of k is readily obtained in the theory if we abandon the circulation of electrons as wholes and ascribe ferromagnetism to a rotation of the electron about its own axis.

For instance, suppose a Lorentz electron (uniformly charged sphere) to be set in slow uniform rotation. The resulting external magnetic field is the same as that of a doublet at the center of moment $M = \frac{1}{3}a^2e\omega$, where a = electronic radius and ω = angular speed; hence the density of electromagnetic momentum at any point outside is $g = EH_\theta/4\pi c = eM \sin\theta/4\pi r^5$, where r = distance from center and θ = angle from axis of rotation. Multiplying by $r \sin\theta$ and integrating throughout the space exterior to the electron one finds as the total angular momentum about the axis of rotation $\Gamma = 2eM/3a$. But the mass is, in our units, $2e^2/3a$. Hence $\Gamma = mM/e$ and $k = 1$.

For the ring electron, according to D. L. Webster's theory $k = 2$. But this result is bound up with the essentially speculative foundation of his theory and it seems certain that electrons of the ring type can be made to give other values to k than 2.

CORNELL UNIVERSITY,
December, 1921.

[1] Phil. Mag., Vol. XLI., p. 279, Feb., 1921.

[2] Ann. der Phys., 60, p. 109, 1919.

Theory of Ionization by Cumulative Action.

By K. T. Compton.

A study of the ionization in a gas subjected to thermionic bombardment between an incandescent cathode and an anode enables certain features of the process of the ionization to be determined. In case of a metallic vapor at more than a couple of millimeters pressure and at moderate voltages, it is readily shown that but a negligible part of the ionization can be due to single direct electronic impacts against atoms. Practically all the ionization is due to ionization of atoms which have previously been partially ionized in the process of producing resonance radiation by a preceding impact or by absorption of such radiation produced by impacts against neighboring molecules.

Under such conditions, and if the thermionic emission is limited by space charge, it is shown that the total number of emitted electrons is:

$$n = \frac{n_0}{1 - 4\sqrt{2}\sqrt{1840 M \pi P_0}},$$

where M is the molecular weight of the gas (on the basis $M_H = 1$), n_0 is the number of electrons which would be emitted under otherwise similar conditions if there were no ionization, P_0 is the probability that any molecule may be in the abnormal or partially ionized condition, and π is a constant which is probably unity for a pure monatomic gas or vapor. By this relation, P_0 may be experimentally determined.

If n_0 be increased, P_0, which increases rapidly with n_0, increases until the thermionic current n would become infinite if it were not limited by the saturation emission at the given temperature. Owing to such limitation, it is shown that the space charge changes sign, with a further increase in current. The maximum arc current cannot exceed two times the saturation value of thermionic emission and, at voltages less than the normal ionizing potential, is probably about one and a half times the thermionic saturation current.

Expressions for P_0 are derived on the assumptions (1) that the abnormal state is the result of a preceding impact against the same molecule and (2) that it results from absorption of resonance radiation. When applied to the particular case of a cathode passing axially inside a cylindrical anode, calculations show that process (2) is much more important than process (1).

This ionization by cumulative action, in which the effect of radiation is very important, is probably of preponderating importance in temperature ionization of gases.

A full report of this work is soon to be published.

Princeton University.

A Significant Exception to the Principle of Selection.

By Paul D. Foote, F. L. Mohler and W. F. Meggers.

The pair $1s-3d$ of sodium and potassium, in Sommerfeld's theory, necessitates an interorbital transition where the change in azimuthal quantum number is two units. The presence of this pair has been always attributed to the incipient Stark effect of the exciting field. In the present paper an experimental arrangement is described wherein the radiation is completely shielded from the applied field—itself only 7 volts. The pair may then be produced at will by increasing the exciting current until it is one of the strongest lines of the spectrum. It therefore is an exception to the selection principle which can not be explained away by a Stark effect. Its explanation is of deeper origin, possibly requiring a reconsideration of the method whereby single azimuthal quantum numbers have been assigned to each of the s, p, d and b terms.

Bureau of Standards.

The Charge on the Alpha Particle.

By J. E. Shrader.

The charge on the alpha particle which is known to consist of two units of electricity has been redetermined by Rutherford and Geiger's method, using the sensitive point and photographic recording apparatus of Geiger.

This method consists essentially of two parts:

1. Measurement of the current due to positive charges from the alpha particles from a given radioactive source.

2. The counting of the alpha particles given off from the same radioactive source.

From the results of these two operations, the charge on the alpha particle and hence the elementary electrical charge has been determined.

Polonium which emits only alpha particles was used as the radioactive source.

The current was determined by the null method with a sensitive quadrant electrometer with an accuracy of about .2 of one per cent.

The counting operation did not give results of comparable accuracy, the error being as great as 4 or 5 per cent. This error is believed to be inherent in the sensitive point method. In operation the sensitive point loses its sensitivity with time and even failure to record is clearly observed. By removal of absorbed gases by electrical heating or by operation of the sensitive point in vacuum, the loss of sensitivity and failure to record are more marked. A failure to record is clearly shown from the fact that the number of particles recorded does not agree with the inverse ratio of the distance and that the number recorded varies with time disproportionate with the rate of decay of the radioactive source.

From observed results, it is believed that the entrance of an alpha particle produces a minute current by ionization by collision and that this stimulates

the release of ionized gas molecules from the point and that this source of ions rather than ionization by collision is responsible for the greater part of the current. Hence the irregularity of counting is due to instability of the gas film.

The value obtained for e by this method taken from an average of several determinations of currents due to positive charges of alpha particles and the number of particles given off from the same source at different rates of counting is 4.78×10^{-10} E.S. units.

The difficulties encountered with the sensitive point method where conditions are hard to control necessarily indicates that this is not a precision method for the determination of e.

Westinghouse Research Laboratory.

Radiation from a Group of Electrons.

By Leigh Page.

The most serious contradiction between Bohr's theory of the atom and classical electrodynamics is in connection with the question of radiationless orbits. Bohr's theory requires the existence of such orbits; electrodynamics seems to deny the possibility of them. To be sure, radiation of the first order can be eliminated by assuming that two electrons revolve in a circular orbit at opposite ends of a diameter, but even in the K ring of an atom of atomic number greater than two (helium) the second order radiation from such a pair is greater than the first order radiation from hydrogen. The object of this paper is to investigate the conditions requisite to the annulment of radiation of all orders. That it is possible to devise an atomic structure involving a finite number of electrons which satisfies all of these conditions is extremely doubtful.

Take some point in the atom (the nucleus) as origin. Let $\mathbf{r}$ be the position vector of an electron relative to this origin. Then, by expanding the retarded expression for the electric intensity due to a point charge, the field strength at a great distance R from the origin is found to have the very simple form (in Heaviside-Lorentz rational units),

$$\mathbf{E}_\infty = \frac{1}{4\pi Rc^2}\left\{\left[\frac{d}{dt}(\Sigma e\mathbf{v}) + \frac{1}{c}\frac{d^2}{dt^2}(\Sigma e\mathbf{r}\cdot\mathbf{M}\mathbf{v}) + \frac{1}{2c^2}\frac{d^3}{dt^3}(\Sigma e\overline{\mathbf{r}\cdot\mathbf{M}}^2\mathbf{v}) + \frac{1}{6c^3}\frac{d^4}{dt^4}(\Sigma e\overline{\mathbf{r}\cdot\mathbf{M}}^3\mathbf{v}) + \cdots\right] \times \mathbf{M}\right\} \times \mathbf{M},$$

where $\mathbf{M}$ is a unit vector having the direction of R, and c is the velocity of light. Hence the conditions for radiationless orbits are

1st order:	$\Sigma e\dot{x}_j = \text{const.}$	3 equations,
2d order:	$\Sigma e x_m \dot{x}_j = \text{const.}$	9 equations,
3d order:	$\Sigma e x_m x_n \dot{x}_j = \text{const.}$	18 equations,
4th order:	$\Sigma e x_m x_n x_0 \dot{x}_j = \text{const.}$	30 equations.

where $x_1 \equiv x$, $x_2 \equiv y$, $x_3 \equiv z$, and the subscripts assume the values 1, 2, 3.

As has been pointed out by Professor Sir Joseph Larmor,[1] and as is evident from these equations, a necessary but not sufficient condition for the absence of second order radiation is that the magnetic moment of the atom shall remain constant.

It is easily shown from these conditions that in the case of a circular orbit in which any even number of electrons are uniformly spaced, the odd conditions are all satisfied. If, however, the electrons are limited to two, none of the even conditions are satisfied, the second order radiation amounting to

$$\frac{8}{5}\beta^2\frac{e^2f^2}{\pi c^3}.$$

If there are four electrons in the ring, the second condition is satisfied, but the fourth and higher even conditions are not, and so on. All conditions are satisfied only when a uniform density of charge is distributed around the ring.

A paper containing the details of the work summarized in this abstract is about to be submitted to the PHYSICAL REVIEW for publication.

YALE UNIVERSITY.

A MAGNETIC FALL OF POTENTIAL METHOD FOR TESTING SHORT BARS OF IRON.

BY ARTHUR WHITMORE SMITH.

THE normal magnetization curves (B–H) for bars of iron 6 x 6 mm. in cross section, and 15 cm. in length, have been accurately determined. In testing short bars it is necessary to use a method in which each part of the iron is subjected to equal values of the magnetic intensity, H. This is the case when the iron is in the form of a thin ring, and when test samples can be obtained only as short bars the conditions of a ring circuit (*i.e.*, without ends or air gaps) should be approximated as nearly as possible.

In the present case the test bar is clamped into a yoke of slightly larger section, which carries the flux out one end of the bar and around to the other end. There are two magnetizing coils. One coil is wound over the yoke, and the other coil is around the bar. Each coil carries a current which can be varied without changing the current in the other coil. When these currents are adjusted so that each coil supplies the magnetomotive force needed to carry the magnetic flux through its part of the circuit, and no more, there is no leakage of magnetic flux at any point along the circuit, and the disturbance due to the end effect is not present.

The difficulty is in knowing just when this condition has been reached. The case is analogous to an electric circuit in which the applied e.m.f. is distributed along the circuit with just enough e.m.f. in each element of resistance to keep the current flowing in that element. All of the points in such a circuit will be at the same potential, although a current is flowing, and a voltmeter joined in parallel with a portion of the circuit will indicate no difference of potential.

[1] Phil. Mag., 42, 595, 1921.

The arrangement that corresponds to a voltmeter consists of a solenoid of many turns of fine wire wound on a fiber core 10 cm. in length. Each end of this solenoid is covered with a plate of soft iron, which extends, on one side, about 5 cm. beyond the side of the coil. These plates are clamped against the test bar at points about 10 cm. apart. The solenoid, with its end plates, thus forms a magnetic shunt in parallel with the middle 10 cm. of the bar. The turns of wire around the bar that are displaced by the plates are wound as near as possible to their proper location to give a uniform winding. The flux through the solenoid is measured with a fluxmeter-galvanometer by the usual method of reversals. No flux through the solenoid indicates that the m.m.f. supplied to the bar is just sufficient to carry the flux through the bar.

This apparatus was used with a bar of ingot iron which had been annealed from 1000° C. in a stream of hydrogen. A ring of the same iron, annealed as nearly as possible in the same way, was also measured for a comparison check. The magnetization curves for the ring and for the bar are practically identical, the small differences being less than might be expected from two rings of the same iron. The agreement is equally good for the smaller values of the flux, where other methods require large corrections.

University of Michigan,
December 10, 1921.
Revised January 12, 1922.

A New Method for the Determination of the Magnetic Susceptibilities of Gases.

By Jakob Kunz and E. C. Fritts.

It has been shown by A. P. Carman and W. Hyslop[1] and by R. Whiddington[2] that the thermionic valve in the heterodyne method of electric oscillations gives an exceedingly sensitive and accurate method for the determination of capacities and dielectric constants. The same method is now applied for the measurement of magnetic susceptibilities of gases. In this case the self-induction of a soil in a vacuum is changed by the introduction of the gas, whose susceptibility has to be measured. We hope to measure in this way not only the magnetic susceptibilities of the ordinary and noble gases, but even of metal vapors and of dissociated gases.

University of Illinois.

A Sine Galvanometer for Determining in Absolute Measure the Horizontal Intensity of the Earth's Magnetic Field.

By S. J. Barnett.

A brief historical statement with reference to the measurement of the horizontal intensity of the earth's magnetic field by magnetic and electrical

[1] Physical Review, 15, p. 243, 1920.
[2] Phil. Mag., 40, p. 634, 1920.

methods is followed by a short discussion of sine and tangent galvanometers, which are the chief instruments used in the electrical methods chosen as simplest and otherwise best.

An improvement in the tangent galvanometer is suggested, but the sine galvanometer is considered preferable, though either one can be constructed in such a way as to satisfy the necessary requirements of speed and precision.

An account is given of earlier sine galvanometers designed for absolute measurements, and a detailed description is given of a new instrument designed by the author and constructed under his supervision on strictly modern lines.

The base of the instrument, including tripod, rough and precision circles, microscopes, etc., was taken from a fine European theodolite and made usable by the substitution of non-magnetic parts for parts too magnetic, and further greatly improved by the substitution of electrical illumination of the precision circle for daylight illumination by mirrors.

The magnetometer-box is of pure copper, the damping being chiefly electromagnetic. The magnet-mirror is a fine disc of chrome steel with optically flat and parallel surfaces, being in fact one of the gages made by the Bureau of Standards. The torsion tube and head are similar to those of the C.I.W. magnetometers. A suspension of phosphor bronze strip with torsional constant about 0.001 is generally used. The telescope is small but powerful; the scale is ruled to thirds of mm., on white pyralin. The period of the magnet and the damping, which is adjustable, are such that readings require only a few seconds.

The coil is double, the arrangement being approximately that due to Helmholtz. The spool was machined from white Carrara marble impregnated with paraffin at a temperature near its boiling point—a process insuring high insulation as well as reversibility of thermal changes. The coils were wound, as suggested by J. V. Jones, under tension in a single layer in spiral grooves, which were cut with a diamond tool. The wire is pure copper, especially prepared by the Research Laboratory of the General Electric Company. Each coil is wound in two halves, as suggested by Ayrton, and contains 10 turns with a diameter of approximately 30 cm. and a pitch of approximately 2 mm. The two halves start from the same horizontal plane 180° apart, so that the distance between centers of adjacent wires is approximately 1 mm. The axial distance between the centers of the two coils, or the distance between corresponding turns of the spirals, is approximately 15 cm. The terminals are so constructed as to have negligible magnetic effects at the center of the coils. The leads are small cylindrical cables with coaxial conductors.

The methods of measuring the diameters and axial distances of the spirals are described and the results are given in tables and curves.

The magnetic tests, of three kinds, proving the materials of construction to be satisfactory, are also described.

The theory of the instrument, the methods of adjusting and using it, and the calculation of the error in the constant of the coils arising from imperfections

of construction, as well as of the other errors introduced in the measurement of the horizontal intensity, are given in sufficient detail.

It is shown that the errors in reading the circle and the scale, when sufficiently large angles are used, and the error in the constant of the coil are quite negligible; and that the only other error necessary to consider, viz., that introduced in the measurement of the current traversing the coils, can also be made entirely negligible. In consequence the horizontal intensity of the earth's magnetic field can be determined with an error less than 1 part in 10,000, which is the precision desired, while the magneticians consider 1 part in 5,000 adequate.

With this instrument it is possible to make several complete determinations of the horizontal intensity in one minute; while at least from half an hour to an hour is required with the magnetometer method.

In addition to the preliminary experimental tests, two considerable series of simultaneous determinations of the horizontal intensity have been made with the sine galvanometer and a standard C.I.W. magnetometer by Messrs. Fleming, Fisk, Peters, Ives, and the author. The intensity variations determined from the galvanometer readings have also been compared with those obtained from simultaneous magnetograms of the Cheltenham Observatory. An account of this work will be published shortly by others. The intensities as determined by the different instruments agreed within 1 part in 25,000, though the errors of the electrical standards used, are not known with a precision such as to justify the expectation of an agreement much beyond one part in 4,000 between the absolute value, even if it were not for the limitations of the magnetometer method.

The complete paper will appear shortly in the *Researches* of this Department.

Department of Terrestrial Magnetism,
Carnegie Institution of Washington.

Results of Comparisons of Instruments for Measuring the Earth's Magnetic Elements.

By Louis A. Bauer and J. A. Fleming.

During the period 1905 to 1921 the Department of Terrestrial Magnetism of the Carnegie Institution of Washington has had the opportunity to carry out intercomparisons of magnetic instruments all over the globe. These intercomparisons have been made at the chief magnetic observatories and at various stations of the Department of Terrestrial Magnetism. Thus the intercomparisons apply not alone to the magnetic instruments as designed and constructed by the Department of Terrestrial Magnetism, but also to magnetic instruments of various designs in use by the chief magnetic services. The resulting data besides yielding the information required for the correlation and reduction of magnetic observations made by existing organizations, have likewise yielded results having important bearings upon the principles and methods of magnetic measurements.

One of the most interesting series of such comparisons was that made recently at the standardizing observatory of the Department of Terrestrial Magnetism between our previously adopted standard magnetometer and a sine galvanometer, designed by Dr. Barnett and constructed in the workshop of the Department. With the latter instrument the value of the horizontal intensity of the earth's magnetic field is determined by an electric method, whereas with the standard magnetometer the same magnetic element is obtained by the usual magnetic method. The results of the comparisons between the two instruments showed satisfactory agreement in the values of the horizontal intensity obtained by the two independent methods.

CARNEGIE INSTITUTION.

FURTHER RESULTS OF LINE INTEGRALS OF THE EARTH'S MAGNETIC FORCE.

BY LOUIS A. BAUER AND W. J. PETERS.

A PAPER was presented by the first author at the joint Chicago meeting of Section B of the American Association for the Advancement of Science and the American Physical Society, on December 30, 1920, giving results respecting possible vertical electric currents cutting the earth's surface. The results were obtained on the basis of the magnetic data accumulated by the Department of Terrestrial Magnetism of the Carnegie Institution of Washington.

The present paper gives additional results as derived from recent computations of line integrals around circuits formed by the tracks of the magnetic-survey vessel, the "Carnegie," and the trips of land expeditions sent out by the Department of Terrestrial Magnetism.

One of the most interesting circuits was that formed by Cruise III of the "Carnegie" in the North Atlantic Ocean, in 1914 extending from New York to 80° north, off the northwest coast of Spitzbergen. This circuit embraces an area of 4,441,176 square kilometers. The result of the line integral around this circuit was such as would be produced by currents of positive electricity passing through the air perpendicularly through the earth's surface of average strength one twentieth of an ampere per square kilometer. For the sake of comparison it may be recalled that the line integral around the United States, as based upon the most recent magnetic data, gives a result which could be produced by currents of positive electricity passing from the air perpendicularly through the earth's surface, having an average strength of about one-thirtieth of an ampere per square kilometer.

From the foregoing it is seen that the results of two line integrals, one over an ocean area exclusively, and the other over a land area exclusively, are of the same sign and are practically of the same magnitude. On the other hand, the vertical currents as disclosed by atmospheric-electric observations, according to present methods over the regions of the two line integrals agree, however, in direction with the results of the magnetic line integrals. Quantitatively, there is a pronounced discordance. The strength of the vertical conduction currents

of atmospheric electricity is only about 1/10,000th of the currents indicated by the magnetic line integrals.

Another circuit for which the line integral has just been computed, is that formed by the track of the "Carnegie's" first cruise made in 1909–10. This circuit encloses an ocean area of 13,050,122 square kilometers and extends from New York to England along the track of ocean travel in latitude about 50 degrees north, thence to Madeira and finally back to New York by way of the sailing routes in latitude 20° north. The result of the line integral around this circuit is the same as that which would be produced by currents of positive electricity passing from the air perpendicularly through the earth's surface and having an average current density of one-twenty-sixth of an ampere per square kilometer. This is practically the same result as was obtained by the evaluation of the line integral around the United States.

Carnegie Institution.

Characteristic X-rays from Light Elements.

By A. Ll. Hughes.

The characteristic x-radiations from the very light elements cannot be studied by the method of crystal analysis, as no crystal is known with spacings between its planes large enough to measure wave-lengths longer than about λ13. To detect the characteristic radiations from the elements under examination, the photoelectric effect of the radiation from the element, when bombarded by electrons, was plotted as a function of the energy of the electrons. A break in the curve was taken to indicate the appearance of characteristic radiation and the corresponding wave-length was inferred from the quantum relation. The element (carbon or boron) was at a distance of less than a millimeter from an incandescent cathode which served as a source of electrons. In the same vacuum was a nickel or silver plate upon which the radiation fell giving rise to the photoelectric effect. Four gauzes at suitable potentials served to prevent the transfer of electrons or ions to the plate giving the photoelectric effect. Breaks were found at 215 volts (λ57.5) and 34.5 volts (λ358) for carbon, and at 148 volts (λ83.5) and 24.5 volts (λ505) for boron. These are the K and L radiations respectively for the elements investigated.

These values can be compared with the theoretical values obtained on extrapolating, by means of Moseley's relation, the known values for the x-ray wave lengths as given in Duane's "Data relating to x-ray Spectra." On extrapolating the values for the $K\alpha_1$ emission lines (and converting into volts), we obtain 275 volts for carbon and 182 volts for boron, and on extrapolating the values for the Ka critical absorption frequencies we obtain 243 volts for carbon and 149 volts for boron. The method employed in this investigation should give values corresponding to the Ka critical points rather than to the $K\alpha_1$ emission lines. The experimental value for boron (148 volts) is in good agreement with the extrapolated Ka value, while that for carbon (215 volts) is lower than the extrapolated value.

Attention is called to the fact that when the square roots of the frequencies of the $K\alpha_1$ emission lines (extrapolated below sodium), are plotted against atomic numbers, the line obtained crosses the line on which lie the square roots of the corresponding critical absorption frequencies (extrapolated below magnesium), between neon and fluorine. That is to say, for elements with atomic numbers below 10, the $K\alpha_1$ emission line would be of *shorter* wave-length than that corresponding to the Ka critical absorption frequency. This is so contrary to the usual views regarding their relative positions, both on theoretical and experimental grounds, that the justification for extrapolation of one or both of these lines must be questioned. It is significant that the reversal of their usual positions takes place just below neon, *i.e.*, their relative positions are only normal down to the element neon, which is the lightest element in which the K shell of electrons is surrounded by a completed outer shell. It is evident therefore that experimental evidence as to the structure of the K radiations for light elements is much to be desired.

The break at 34.5 volts for carbon, corresponds to $\lambda 358$, which is just below shorter than the shortest of the L emission lines in the spectrum of carbon as found by Millikan, as it should be if it is the L critical absorption point.

QUEEN'S UNIVERSITY,
KINGSTON, ONTARIO.

ENERGY RELATIONS BETWEEN X- AND β-RAYS.

BY J. A. GRAY.

EXPERIMENTS have been carried out with the β-rays of radium E in order to determine the relative amounts of energy in the x-rays formed by these β-rays when they penetrate different materials. Paper, iron and lead were the materials used. In making the determinations, it has been assumed that the energy in a beam of x- or β-rays is proportional to the total ionization produced by the beam in air.

If a beam of β-rays of energy E_1, strikes a plate so thin that an inappreciable number of them is scattered by the plate, and x-rays of energy E_2 are formed in the plate we may write

$$E_2 = \lambda E_1 m,$$

where m = mass per unit area of the plate. The quantity λ may be called the mass transformation coefficient. The following values of it have been found: for carbon it equals 0.047, iron 0.110 and lead 0.300. These numbers are in the proportion 1 : 2.3 : 7.2.

When the β-rays of radium E are completely absorbed by paper 0.4 per cent. of their energy is transformed into energy of x-radiation. The corresponding values for iron and lead are 1.35 per cent. and 6 per cent. respectively. These numbers are in the proportion 1 : 3.4 : 15. It is known that when scattering is taken into account, β-rays can pass through a greater mass of materials of

high atomic weight than of materials of low atomic weight. The numbers given above show this, and indicate that the "mass" range of β-rays is about 15/7.2 times or twice as great in lead as in paper.

From the results it can be shown that, in general, secondary β-rays after their expulsion can only give rise to a negligible proportion of the secondary x- or γ-rays formed when a primary beam of x- or γ-rays pass through matter.

McGill University.

Positive Ray Analysis of Zinc and Calcium.

By A. J. Dempster.

Further experiments with zinc have shown that large variations occur in the proportions of the four components observed.[1] This makes the reasoning invalid in which the atomic weights were deduced to be 63, 65, 67 and 69, in order that the mean weight might agree with the chemical atomic weight 65.4. With calcium anodes to which a little zinc had been added, it was found possible to obtain the calcium and zinc lines at the same time and compare their atomic weights. The zinc lines were thus found to have the atomic weights 64, 66, 68 and 70. This makes zinc agree with the rule observed to hold in the isotopes of the inert gases, that even atomic weight usually goes with even atomic number. The strong calcium line at 40 was compared with a potassium line at 39 and a magnesium line at 24. With calcium a weak component was observed with atomic weight 44. This is provisionally considered to be a real isotope and not due to carbon dioxide, since any calcium carbonate present should be dissociated at a lower temperature than that used.

University of Chicago.

The Effect of Dissolved Substances on the Deposition of Colloidal Particles from a Solution by Means of an Electric Current.

By Richard D. Kleeman.

During some experiments on the electric deposition of porcelain slip it was observed that the closeness of the particles of the deposit obtained was affected by a small quantity of a substance dissolved in the slip, the magnitude of the effect depending on the nature of the substance dissolved. Thus for example, the deposit obtained from a slip containing about 1/300 of its weight of sodium silicate (Na_2SiO_3) is hard though not quite dry, while that obtained without the admixture of sodium silicate is of a semi-liquid consistency like cream. Similar results were obtained with Na_3PO_4, Na_2HPO_4, Na_2SO_4, H tartrate, Na tartrate, NaOH, KOH, and in fact most substances show the same effect in a more or less degree.

The effect was found to be closely associated with the increase in fluidity

[1] Physical Review, (2) xix., p. 271.

of the slip obtained on adding a small quantity of one of these substances. This permits a considerable amount of colloidal matter to be added to the solution with the substance, without a change in the fluidity, the amount of matter added affording a sort of measure of the increase in fluidity introduced by the dissolved substance. The latter effect is known and is used to obtain a concentrated porcelain slip for casting in the wet porcelain process by the addition of a small quantity of sodium silicate. It was found that the increase in compactness of the deposit on adding a small quantity of the foregoing substances was attended by an increase in the fluidity of the solution.

These two effects and their association may be explained by supposing that the dissolved substance decreases the "radii of the spheres of action" of the colloidal particles. The particles would accordingly, on addition of the substance, have additional room for motion with a resultant increase in the fluidity in the solution, and would pack more closely on being deposited by an electric current. A theoretical investigation along these lines is given.

It is evident that if the radii of the spheres of action of the particles are decreased sufficiently spontaneous precipitation would result. Thus it would follow from the foregoing results that a substance which precipitates a colloidal solution, if added in an appropriate amount, should in all cases increase the fluidity of the solution and increase the compactness of the deposit obtained with an electric current.

RESEARCH LABORATORY,
GENERAL ELECTRIC COMPANY,
SCHENECTADY, N. Y.

THE EFFECTIVE RANGE OF β-RAYS.

BY J. A. GRAY AND A. V. DOUGLAS.

WHEN plates of any substance are placed over a source of β-rays, a thickness of the substance will eventually be reached such that none of the original β-rays will pass through it. The smallest mass per unit area of the substance which will satisfy this condition is called the effective range of the β-rays in that substance. It is called effective range owing to the fact that, through scattering, β-rays really have a greater total path than that indicated by these measurements. Mass per unit area is taken instead of thickness so as to compare different substances.

This range has been obtained by using an electroscope to give a measure of the intensity of the β-rays. The source of β-rays was an active preparation of radium (D + E). The effective range of these β-rays has been found in paper, aluminium, copper, tin and lead. In paper the range is 0.47 gramme, in lead 0.34 gramme, the range being inversely proportional to what has been called the mass absorption coefficient of the β-rays.

The range in paper has also been obtained of rays scattered through large angles by sheets of silver and lead. Although the rays examined are slower, on the whole, than the primary rays, there is a strong indication that β-rays

lose only a small proportion of their energy, when they are scattered through large angles. It is difficult to be quite certain that they lose any at all, because the scattering of β-rays is not a surface effect.

The effective ranges of secondary β-rays excited in lead by different types of x- and γ-rays have also been determined and are being found useful in problems connected with the transformation of β-rays into x-rays and vice versa.

McGill University.

On the High Frequency Rays in the γ-ray Spectrum of Radium B and C.

By Alois F. Kovarik.

The method described was devised for the study of the spectra of soft γ-rays, for example, the γ-rays from radium DE—an investigation which is planned by the writer. However, since the penetrating radiations offer a better chance to test the method and also because the only work on record on the γ-ray spectrum of radium is by the photographic method [1] it was thought advisable to study at first the spectrum of the γ-rays from radium B and C. The work here recorded is preliminary to a study of the whole spectrum and bears on the high frequency radiations alone.

The source of the radiations was a standard radium salt of 1.3 milligrams radium content. The radium was placed in the center of a lead block 15 cm. on the edge and the rays passed through an opening in this block and through a slit 1 mm. wide and 6 cm. deep in another block of lead placed in front of the former. The rays fell on a crystal of calcite and were reflected into a point discharge counting chamber after passing through a slit 0.5 mm. wide and 7 cm. deep placed in front of the counting chamber. The counting chamber was also surrounded by lead. The crystal and the counting chamber were moved together, the latter through double the angle of the former and the discharges produced in the counting chamber by the γ-rays entering through the slit (and otherwise) were automatically registered using the device previously described by the writer.[2]

The principal lines recorded by Rutherford were verified but other lines were also detected. Among these, it is of especial interest to note that there are at least five and possibly more lines of shorter wave-length than the shortest one (43′ from rocksalt) reported by Rutherford and Andrade. The glancing angles from calcite of these lines are 41′ (corresponding to the 43′ from rocksalt), 37.5′, 33′, 27.5′, 21′, and 16′.

The study will be carried on, using crystals of various kinds and also of various thicknesses. The method is applicable in particular to the study of rays from weak sources, as is seen from the present case in which only a little more than a milligram of radium was used.

Yale University.

[1] Rutherford and Andrade, Phil. Mag., 27, 854; 28, 263, 1914.

[2] Kovarik, Phys. Rev., (2), xviii., 272, 1919.

THE BEGINNING OF THE K AND L SERIES OF X-RAYS.

BY F. L. MOHLER AND PAUL D. FOOTE.

MEASUREMENTS of radiation from a thermionic discharge in gases and vapors have been made by means of its photoelectric effect on electrodes within the same tube but electrically shielded from the discharge. This radiation current is nearly a linear function of the voltage across the arc with changes in slope at the critical potentials. A previous paper[1] gave measurements for some metallic vapors that showed critical potentials due to the softest x-rays of these elements.

Measurements have now been extended to twelve elements and compounds from which can be identified the L limits of five elements in the second row of the periodic table and the K series for four in the first row. The gases and vapors used were BCl_3, CO, CO_2, C_2H_4, CCl_4, Air, O_2, Na, Mg, P, S and K. The last showed M limits given in the above-mentioned paper.

The L limits can be identified by the agreement with values computed from the observed K spectra. We find not only the principal L limit

$$La_{1,2} = Ka - K\alpha_{1,2}$$

but potentials corresponding to the hitherto unknown limits,

$$La_{5,6} = Ka - K\alpha_{5,6}$$

and in one or two cases

$$La_{3,4} = Ka - K\alpha_{3,4}.$$

Element.	Z.	Observed Potentials Volts.	K Limits λ in A.	L Limits Observed λ in A.	L Limits Computed λ in A.
Boron	5	186	66.4		
		125			
Carbon	6	272	45.4		
		234			
Nitrogen	7	374	33.0		
		352			
Oxygen	8	478	25.8		
Sodium	11	35		353	
		17		725	
Magnesium	12	46		268	263
		33		374	303 422
Phosphorous	15	126		98	92.2
		110		112	103
		95		130	
Sulphur	16	152		81.2	77.1
		122		101	99.9
Chlorine	17	198		62.3	61.9
		175		70.5	
		157		78.6	

[1] Abs. PHYS. REV., 18, p. 94; 1921.

A plot of the square root of these frequencies against atomic number gives three nearly parallel straight lines.

The potentials ascribed to the K limits likewise give a straight line. It is interesting to note that the ionization potential of He falls on the K line and that of Ne on the principal L line. The table gives only critical potentials that fall in the region of x-ray limits. It must be emphasized that the experimental errors in "computed L limits" are of the same magnitude as for the observed points.

Bureau of Standards.

Secondary X-rays from Crystals.

By G. E. M. Jauncey.

Using a Bragg x-ray spectrometer, the crystal was fixed at a certain angle and the ionization chamber was set at a series of angles between an angle $A°$, which was near zero, and 90°. The slit in front of the ionization chamber subtended an angle of 6° at the center of the table, while the angular width of the beam of primary x-rays incident on the crystal was less than 0.25°. Using the general radiation from an x-ray tube with a tungsten target, it was found that, although the maximum deflection of the electrometer occurred when the angle of the ionization chamber was double that of the crystal, yet the deflection was quite appreciable at other angles of the ionization chamber.

From the curve showing the relation between the intensity at various angles and the angle of the ionization chamber, the value I_s of the total intensity of radiation emitted by the crystal between the angles of $A°$ and 90° in the plane of reflection was calculated. The ratio of I_r to I_s, where I_r is the intensity at the position of reflection, is shown in the following table:

Rocksalt Crystal.

Crystal Angle Degrees.	Angle A Degrees.	I_r/I_s Per Cent.
7	7	33
10	10	19
15	15	18

From the table it is seen that the reflected radiation constitutes less than one half of the total radiation emitted by the crystal. There is radiation at all angles up to 90°, the regularly reflected radiation being added to that which is radiated at all angles.

Setting the crystal at an angle of 7° and the ionization chamber at 60°, the absorption produced by 3 mm. of aluminium when placed in the primary and then in the secondary beam was determined. In the primary beam the aluminium reduced the intensity to 46 per cent., while in the secondary it

reduced the intensity to 42.5 per cent. There seems, therefore, to be some fluorescent radiation present.

WASHINGTON UNIVERSITY,
ST. LOUIS, MO.,
December 12, 1921.

BRIGHTNESS OF TUNGSTEN.

BY W. E. FORSYTHE.

THE brightness of tungsten in candles per square centimeter has been measured by three different methods for a wide range of temperatures. The first method used was the direct one where the light from a definite length of a filament of a known diameter was measured for a temperature of about 2350° K. and from the values thus obtained the brightness per square centimeter calculated. Values were thus obtained using special 20-mil. tungsten lamps and also special lamps with a ribbon filament several centimeters long, 2 mm. wide and about .01 mm. thick. Values of the brightness for points a few hundred degrees above and below this were obtained in terms of this value by direct comparison. By this method the brightness was measured from 2080° K. to 2600° K.

The second method was to use as a brightness photometer a disappearing filament optical pyrometer having for the monochromatic screen a yellow-green glass whose effective wave-length for the different temperature intervals was very close to the Crova wave-length for the same temperature intervals. This pyrometer was calibrated for brightness from a black body. Since both the Crova wave-length and the effective wave-length of the screen used, as well as the different temperature intervals over which measurements were made were known, it was possible to correct values of brightness obtained to the values that would have been obtained if the Crova wave-length had been used in each case. By this method the brightness was measured from about 1000° K. to about 3400° K.

The third method was by calculation using the following relation involving the brightness of the black body, the color temperature (Tc) and brightness temperature (S) of the tungsten.

$$B_w = B_{BB} \cdot \frac{e^{-\frac{c_2}{\lambda S}}}{e^{-\frac{c_2}{\lambda Tc}}},$$

where B_{BB} is the brightness of a black body at a temperature $T = Tc$. By this method values were obtained for a temperature range from about 1000° K. to the melting point of tungsten. The three methods gave results that agreed well within the experimental error. The values obtained were plotted log B_w against log T and from the smooth curve the values given in the table were obtained.

The true temperatures (T) of the tungsten used were calculated from the brightness temperatures and the emissive powers given by Worthing.[1] The values of the brightness given in the table are on the scale of candle-power adopted by the Bureau of Standards. The values of the brightness given agree well with those given by Langmuir[2] when the difference in the temperature scale is taken into account and account is taken of the fact that Langmuir's values are not on this scale of candle-power. From the smooth curve between log B and log T the change in brightness due to a change in temperature was obtained for the different temperatures and the values given in the third column of the table. As might be expected these values of the relative change are about the same as are obtained from the black body.

Table I.

Brightness and Variation in Brightness at Various Temperatures.

Temperature °K.	Brightness Candles per Square Centimeter.	Per Cent. Change in Candle-power for One Per Cent. Change in Temperature.
1000	.000098	27.0
1200	.00585	21.6
1400	.1075	18.1
1600	.925	15.6
1800	5.21	13.7
2000	20.1	12.3
2200	61.7	11.2
2400	155.5	10.3
2600	343	9 5
2800	679	8.9
3000	1235	8.4
3200	2105	8.1
3400	3380	7.9
3600	5200	7 8

Nela Research Laboratory of Pure Science,
Cleveland, Ohio.

The Luminescence of Solidifying Antimony.

By E. Karrer.

When antimony is heated to a temperature above its melting point (630° C.) it becomes bright red. If it is then allowed to cool, its brightness will decrease with the temperature down to the point where solidification sets in, where a sudden increase in brightness occurs. The temperature also increases at this point. The phenomenon is therefore very similar to recalescence in iron. The brightness after the flash appears greater for a given temperature than the brightness at the same temperature before the flash. Thus it appears from this fact to be a case of crystal-luminescence.

[1] Physical Review, (2), x., p. 389, 1917.

[2] Physical Review, (2), vii., p. 302, 1916.

The phenomenon is not due to the oxidation of the antimony since it takes place in hydrogen and in vacuum.

One sample of bismuth showed the same phenomenon occurring at the same temperature. This was due to contamination of the bismuth. Roughly one part of antimony in 2,000 of bismuth is sufficient to show luminescence.

Details will appear in Journal Am. Opt. Soc.

NELA RESEARCH LABORATORIES,
CLEVELAND, OHIO,
December, 1921.

THE THERMIONIC WORK FUNCTION OF TUNGSTEN.

BY C. DAVISSON AND L. H. GERMER.

IN the derivation of Richardson's equation, $i = AT^{1/2}\epsilon^{-b/T}$, the constant b is related to the energy, Φe, required to liberate a single electron through the equation, $\Phi e = bk$, where k is Boltzmann's gas constant and e the electronic charge. Φ is referred to as the equivalent voltage of the work function.

The authors have made a direct calorimetric determination of Φ upon a filament of pure tungsten by the measurement of changes arising from the cooling effect of the emission. At the same time the b of Richardson's equation has been determined, and the calorimetric Φ has been compared with bk/e. With the exception of some work done on oxide-coated platinum filaments by W. Wilson[1] this is the first measurement of these two constants ever made upon the same filament.

The value of Φ has been computed from the relation,

$$\Phi = \frac{2EI}{E - I\dfrac{dE}{dI}} \cdot \frac{\Delta E}{i},$$

where ΔE is the change in voltage across the filament caused by the emission, i, while the heating current, I, is maintained constant. All essential measurements were made upon a Leeds and Northup potentiometer. After correcting for several spurious effects our final value is

$$\Phi = 4.91 \pm .05 \text{ volt.}$$

For the determination of b the temperatures of the filament must be accurately known. The calculation of these temperatures has been based on the temperature characteristics of tungsten published by Langmuir and by Worthing and Forsythe. Langmuir's data lead to a value of b equal to 5.646×10^4 degrees, while those of Worthing and Forsythe lead to the value 5.541×10^4 degrees. The relation between resistivity and power radiated per unit area for the filament used in the present experiment was found to be accurately consistent with Worthing and Forsythe's data. Furthermore, the temperature scale of Worthing and Forsythe is probably more accurate than the scale of

[1] Nat. Acad. of Sci. Proc., 3, p. 426 (1917).

Langmuir. From both of these considerations it is believed that the latter value of b is the more reliable.

The derivation of Richardson's equation, with the assumptions involved, requires that the values of Φ and of bk/e for a given material be identical. The values of b given above correspond to values of bk/e that are, respectively, 0.8 per cent. and 2.7 per cent. lower than the calorimetrically determined Φ. Since the value of b, corresponding to the greater of these discrepancies is regarded as the more reliable, a real, though small, difference between the constants is indicated. There is some question, however, as to what probable error should be assigned to the values of b. For this reason we do not feel that a difference between Φ and bk/e can be regarded as definitely established.

Research Laboratories of the
American Telephone and Telegraph Company
and the Western Electric Company, Inc.

A Spectroscopic Method for Determining the Effective Temperature of Absorbing and Emitting Molecules.

By Raymond T. Birge.

In a preliminary investigation[1] of the distribution of intensity in typical band series, as affected by temperature, it was found that Kemble's formula for the statistical distribution of angular velocities did not exactly represent the intensity distribution. This is to be expected, since the intensity, on the quantum theory of band spectra,[2] should be given by $I = (E - E')B_m'^m(a_m)$. If this expression refers to absorption spectra, then, labeling the missing line $m = 0$, the value of m for any line refers to the number of quanta of angular momentum in the initial state.[3] The third factor, a_m' then gives the distribution of angular momentum, and if "J" is a constant, the distribution of angular velocities as well. On this assumption Kemble's formula is the theoretical expression for a_m.

Now $E - E' (= h\nu)$ varies only slightly throughout a band. $B_m'^m$, from the author's curves of intensity distribution, varies slowly with m, if m is not too small. The moment of inertia of the molecule in its initial condition (J) can be obtained from the coefficient of the first power term of the Deslandres' formula for the series considered.[4] The deviations of the CN series from a parabolic law show that J is not constant, but that it is approximately so.

The value of m corresponding to maximum intensity, in Kemble's formula, is

$$m_m = \frac{2\pi}{h}\sqrt{kJT},$$

where k is the gas constant per molecule. This connects m with the absolute

[1] Phys. Rev., 18, 319, 1921.

[2] Heurlinger, Zeit. f. Physik, 1, 82, 1920.

[3] Kratzer, Zeit. f. Physik, 3, 289, 1920.

[4] See Sommerfeld's Atombau, 2d edition, p. 555.

temperature of the absorbing or emitting gas, with the approximations mentioned. These approximations are such as to have little effect on the position of m_m, although they decidedly affect the form of other parts of the intensity curve. Introducing the known values for the A series of the 3883 CN band, we have $T = 5.5m^2$.

In active nitrogen,[5] m_m is estimated to be at 9 ± 2. For the 4216 band,[1] for which J is the same, I estimate m_m at $8 \pm 1\frac{1}{2}$. This latter figure gives $T = 80°$ C. $\pm$ 150°. The actual temperature is believed by investigators to be somewhere between room temperature and 100° C. In King's 2700° furnace spectra, m_m should be 23.25,—in the 2500° spectra, 22.45. In each case I find it to be 23 ± 2. (This result has been obtained with far greater care than the preliminary value of 22 previously published.[2])

Assuming then the approximate validity of the formula, we obtain for King's 4 amp. arc a temperature of 4000° C. $\pm$ 300° (from $m_m = 28 \pm 1$), and for my 13 amp. arc 4700° C. $\pm$ 300° (from $m_m = 30 \pm 1$). These values are consistent with previous estimates of the temperature of the arc. A spectrogram taken by King, showing the 3883 band in absorption at about 3000° C. indicates, as nearly as can be judged, that the intensity distribution in absorption is the same as in emission, at the same temperature. Assuming this, an examination of a solar spectrogram lent by Dr. St. John indicates an effective temperature for the CN (or possibly N_2) molecules of the reversing layer of the sun probably hotter than King's arc, and as nearly as can be judged, the *same* as the 13 amp. arc, *i.e.*, 4700° C. This estimate is probably too low, if anything, due to the approximations used. It is believed however that this method can be employed for the quantitative determination of effective solar temperatures.

PHYSICAL LABORATORY,
UNIVERSITY OF CALIFORNIA.

THE EXCITATION OF THE ENHANCED SPECTRA OF SODIUM AND POTASSIUM IN A LOW VOLTAGE ARC.

BY PAUL D. FOOTE, W. F. MEGGERS, AND F. L. MOHLER.

THE enhanced spectrum of sodium and its L-radiation are excited at about the same voltage. Similarly, the M-radiation and the enhanced spectrum of potassium appear simultaneously.

The highest frequency in the simply enhanced spectrum of sodium is estimated to be in the neighborhood of 14 volts and of potassium, 11 volts.

The evidence confirms the theories of Bohr and Sommerfeld which attribute enhanced lines to the ionized atom, and arc lines to the neutral atom.

The following table summarizes the values of the critical voltages characterizing the three-stage development in the spectra of sodium and potassium.

[1] Strutt and Fowler, Proc. Roy. Soc., A86, Plate op. p. 117, 1911.

[2] All the results here quoted were obtained before their quantitative theoretical significance was realized. They are therefore unbiased in this respect.

Element.	Volts.	Notation.	Spectrum.
Sodium.....	2.09	1s–2p	Single pair
	5.11	1s	arc lines,
	35–30	...	enhanced lines and L-radiation $L_a = 35\ L_a$
Potassium.....	1.60	1s–2p	Single pair $= 30$
	4.32	1s	arc lines,
	$\{23$ 20	...	enhanced lines and M-radiation.

Highest frequency in enhanced spectrum: sodium = 14 volts; potassium = 11 volts. Total work of double ionization: sodium = 49 volts: potassium = 34 volts.

Bureau of Standards.

The Significance of the 1/2 Terms in Spectral Series Formulæ.

By Paul D. Foote and F. L. Mohler.

Sommerfeld showed that the relation between the Ritz series constant a for the arc spectra of the alkalies and a^* for the spark spectra of the alkali earths was of the form $a^*/a = 2$. To verify this for the $m\mathfrak{S}$ and ms terms it was necessary to assign half integral values to m. However, by postulating two rings of electrons, the outer ring containing the generally accepted number of electrons, 8, 18, etc., and considering the shrinkage of the rings when the nuclear charge is increased, the computed ratios a^*/a run from 1.48 to 1.66 and are closely satisfied by $\mathfrak{S}$ and s if to m we assign integral values. The simple physical conceptions of the quantum theory suggest that m should be an integer and in the present paper as good evidence is offered confirming this viewpoint as has been advocated to the contrary.

Bureau of Standards.

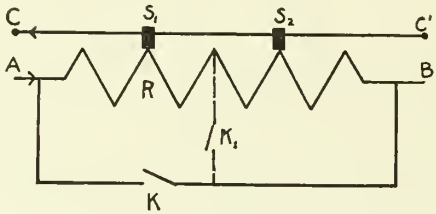
A Method for Increasing the Carrying Capacity of a Rheostat.

By W. E. Forsythe.

When using an ordinary slide resistance to control a current it often happens that when the current is the largest only a small part of the resistance is being used. This may be disadvantageous for two reasons: In the first place, the smallest change possible in this small part of the resistance may greatly increase the current and in the second place, the resistance may be very much overheated. To overcome these difficulties a method has been devised whereby it is possible to use both ends of the rheostat and thereby double its carrying capacity and at the same time make current control easier and more accurate. In Fig. 1 is shown diagrammatically a slide rheostat with the additions necessary in order that both ends can be used.

The current ordinarily enters at the binding post A, passes through the resistance R and out at the binding post C through the slide CC'. As the slide

S_1 is moved towards A to increase the current, more and more of the resistance is cut out of the circuit and is not used. To change the rheostat so as to double its carrying capacity put on a second slide, S_2, a second binding post, B, at the end of the rheostat opposite A and a switch, K, so connected that when it is closed the two binding posts, A and B, are connected. To operate the rheostat proceed in the ordinary manner (switch K open) with the current entering at A passing through the resistance R, the slide S_1 and out at C. To increase the current move this slide towards A until it has passed over three fourths of the distance from B to A. To obtain a larger current move both slides to the center of the resistance R and close the switch K. The resistance will be about the same as it was with one slide and one-fourth of the resistance in use. The current will be divided at A and one half of it will enter at B and pass out at S_2, the other half entering at A and passing out at S_1. To increase the current move either slide S_1 towards A, slide S_2 towards E, or move the two slides farther apart.



Two such rheostats have been made in Nela Research Laboratories and used regularly for a year or more and found convenient to control a current of fifty to sixty amperes with a rheostat originally constructed to carry but thirty.

This plan can be carried a step further by introducing another switch K_1 as shown by the dotted line in Fig. 1 and by adding two more contacts.

NELA RESEARCH LABORATORIES, CLEVELAND, OHIO,
April, 1921.

A TRANSITION OR ADSORPTION LAYER THEORY OF THE E.M.F. OF THE VOLTAIC CELL.

BY RICHARD D. KLEEMAN.

A METAL plate immersed in a liquid or solution necessarily gives rise to a transition layer in the immediate vicinity of the plate in which the density of the liquid is different from that in the interior of the liquid, due to the nature and magnitude of the molecular forces to which the elements of the liquid are subjected, being different near the plate from what obtains at other parts. In the case of a solution this may give rise to a different density of the solute in the layer, which is known as adsorption. If the solute is an electrolyte the dissociation in the layer would therefore be different from that in the interior of the solution, and would vary from one part of the layer to the other. Due to the different rates of diffusion of the positive and negative ions an electric field would accordingly be set up across the layer. The formation of this field

would be attended by a charging up of the plate. Ultimately equilibrium of the ions in the solution would exist under the electric field due to the *charge on the plate*, and the field due to the *separated charges of opposite signs in the solutions*.

A difference of potential would accordingly exist between the interior of the metal plate and the remote side of the solution. The differential equations of this potential can be formed and are given in the paper. It is also proposed that the e.m.f. of a cell arises entirely in the foregoing manner. Various consequences that follow from this proposition are pointed out and discussed.

If the difference of potential of the *separated charges* in the solution is small in comparison with that due to the *charge on the plate*, as may occasionally be the case, we would be dealing with a case covered by Nernst's solution pressure theory of the e.m.f. of a cell. It appears therefore that the theory proposed by the author would explain the "mechanism" of Nernst's solution pressure in those cases where his theory is applicable. And in the cases where it cannot be applied without difficulties being introduced, as for example happens when the nature of each electrode is different from that of the deposit obtained on it on allowing an electric current to flow through the system, the theory proposed simply explains the e.m.f., and besides explains the change in the e.m.f. caused by the polarization of the electrodes.

Union College,
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Quantum Theory of Photographic Exposure.

By Ludwik Silberstein.

The author assumes that the light impinging upon the photographic plate consists, either in part or entirely, of discrete light quanta, and that the necessary and sufficient condition for a silver halide grain to be "affected" by light, *i.e.*, to be made developable, is that it should be fully hit by and absorb a light quantum. The question is thus reduced to a problem in probabilities. For moderate numbers of grains and of light quanta the number of silver halide grains affected is represented by a harmonic series, which for large numbers of the former leads to an exponential formula, valid for each size (area)-class of grains separately. The exponent is proportional to the size of the grain and, for light quanta of non-negligible section, is a function of the wave-length showing a maximum. *Cæteris paribus*, the "speed" of a photographic plate is thus shown to increase with the size of the grain; at the same time the maximum sensibility shifts towards the red end of the spectrum. The available photographic data seem to corroborate characteristically some of the consequences of the theory. Other consequences, with all their quantitative details, are being subjected to special sensitometric, microscopic, and spectrophotometric tests now in progress in the Eastman Laboratory. Three sets of exposures gave a striking agreement with the formula.

The Physical Constituents of the Atmosphere of Venus.

By Chas. E. St. John and Seth B. Nicholson.

The literature on planetary atmospheres is permeated with the assumption that the atmosphere of Venus is similar to our own, in particular as to the presence of oxygen and water vapor. This assumption rests upon spectrographic observations with low dispersion in which an increased intensity of the terrestrial lines was thought to be seen in spectra of Venus. Spectrograms of Venus with a dispersion of 3 Å. per mm. when the relative velocity was sufficient to separate lines due to atmospheric absorption in Venus from the corresponding terrestrial lines show, however, no trace of lines in the positions in which the Venus components should appear. From comparison with laboratory observations it is deduced that companions to the terrestrial lines should have been detected, if the light had penetrated a layer of oxygen on Venus equivalent in radial depth to 3 meters of oxygen under normal conditions.

In the depth penetrated in the planet's atmosphere there was then less than one five-hundredth part of the amount of oxygen in the earth's atmosphere.

As to water vapor it is deduced that if the solar beam had traversed, in and out, one millimeter of precipitable water, the water-vapor lines would have been doubled.

According to Jewell's observations the water vapor in the atmosphere over Baltimore is equivalent to 40 mm. of water. Moore gives it as about 50 mm. for the ordinary American climate.

Mount Wilson Solar Observatory.

The Separation of Mercury into Isotopes.

By William D. Harkins and R. S. Mulliken.

The paper reports the details of the apparatus used in a separation of the isotopes of mercury amounting to 127 parts per million. It is found that the separation attained varies as the logarithm of the cut and as the square of the difference of atomic weight (when there are only two isotopes), and inversely as the mean atomic weight.

University of Chicago.

The Crystal Structure of Mercury.

By L. W. McKeehan and P. P. Cioffi.

The crystal structure was determined by the "powder" method developed by A. W. Hull,[1] and with standard equipment for the use of molybdenum x-rays obtained from the General Electric Company. The low temperature required to keep the mercury frozen was obtained by boiling liquid air by an electric heater in a small vacuum flask and allowing the vapor to escape through

[1] Phys. Rev. (2), *10*, 661 (1917).

a glass tube in which the cylindrical sample was mounted axially. A temperature of about $-115°$ C. was thus maintained. To prevent the deposit of ice crystals on the air conduit it was made double walled with vacuum heat insulation. The sample itself consisted of a thin coat of minute mercury droplets condensed on the outer surface of a paraffin- or shellac-coated glass capillary tube mounted in metal bearings and provided at one end with a light screw propellor. The cooling air thus supplied the motive power for rotating the sample. Since much of the radiation utilized had to traverse six thicknesses of glass, the thinnest practicable walls were used and pyrex glass was chosen, further, to minimize absorption. Even so, exposures up to nearly thirty hours were required with 30–35 milliamperes through the x-ray tube, and the photographs are too faint for easy reproduction.

Preliminary trials, using the plots furnished with the apparatus[1] showed the best fit with a rhombohedral lattice with the axial ratio 1.94. It was assumed in the calculations that the agreement between the spacings of (111) and (110) planes was exact, which requires

$$\lambda = \cos^{-1} \tfrac{1}{3} = 70° - 31'.7,$$
$$C = \tfrac{1}{2}\sqrt{15} = 1.9365,$$

and gives a pattern of great simplicity. The tabulated values include all the

Miller Indices.	Theoretical Spacings.	Observed Spacings.		Relative Intensity Estimated.
		No. 1.	No. 2.	
	$a = 3.025$			
	$\lambda = \cos^{-1}(\frac{1}{3})$			
100	2.761	2.760	2.771	8
111	2.250	2.245	2.255	10
100				
$10\bar{1}$	1.747	1.748	1.750	6
$11\bar{1}$	1.476	—[2]	1.474	4
211				
210	1.381	1.382	1.379	2
100(2)				
221	1.235	1.255	1.235	2
$20\bar{1}$				
111(2)	1.127	1.125	—	1
110(2)				
$21\bar{1}$	1.083	1.085	—	1
$2\bar{1}\bar{1}$	1.008	—	1.035	1
311				
321	0.947	—	0.943	1
310				

[1] A. W. Hull and W. P. Davey, Phys. Rev. (2), 17, 549 (1921).

[2] Bad spot on film too close to estimate position of line.

Rhombohedral System: $\lambda = 70° 31'.7$, $a = 3.025 \times 10^{-8}$ cm.
Hexagonal System: $C = 1.9365$, $a = 3.493 \times 10^{-8}$ cm.
Atomic volume: 23.82×10^{-24} cm.^{3},

distinct lines on the two best photographs, and show excellent agreement with the assumed structure. The calculated density if one atom is associated with each cell (simple rhombohedral lattice) is 13.97 gm./cm.^{3} If the value of Mallet[1] for the density of solid mercury at its melting point, 14.193 gm./cm.^{3}, and that of Dewar[2] for its density in liquid air, 14.382 gm./cm.^{3}, are accepted, the density at $-115°$ C. should be about 14.29 gm./cm.^{3}, which differs from the value here determined by considerably more than its probable error, and may indicate that a closer packing of atoms can occur in large ingots than in microscopic droplets.

The other members of the group to which mercury belongs are magnesium, zinc, and cadmium, all of which form close packed hexagonal lattices, the axial ratio increasing from that appropriate to spheres, 1.624 in the case of magnesium[3] though 1.860 in the case of zinc,[4] to 1.89 in the case of cadmium.[4] The structure of mercury here found is not a close packing for spheroids, and is the first simple rhombohedral arrangement obtained for an elementary substance.

RESEARCH LABORATORIES OF THE
AMERICAN TELEPHONE AND TELEGRAPH CO.
AND WESTERN ELECTRIC COMPANY, INC.
December 14, 1921.

[1] J. W. Mallet, Roy. Soc. Lond. Proc., *23*, 71 (1877).
[2] J. Dewar, Chem. News, *85*, 277 (1902).
[3] A. W. Hull, Nat. Acad. Sci. Proc., *3*, 470 (1917).
[4] A. W. Hull, PHYS. REV. (2), *17*, 571 (1921).

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THE

PHYSICAL REVIEW.

RESISTANCE AND THERMO-ELECTRIC POWER OF METALLIC GERMANIUM.[1]

By C. C. Bidwell.

Synopsis.

Electric Resistance and Thermo-electric Power of Germanium, from − 191° to 675° C.—Measurements were made on a pure specimen of this rare metal in the form of a rod 2.4 by 0.44 by 0.41 cm., prepared under the direction of L. M. Dennis. The current was led in through graphite blocks and thermo-junctions were placed in grooves near each end. For the thermo-electric power determinations a temperature gradient was secured by placing the specimen in a non-uniform part of a furnace or refrigerator and also by using a heater coil wound on one end. Between 125° and 450° the results indicate a slow reversible transformation of some sort, for below and above this range the thermo-electric power is a linear function of the temperature and also, except in the range 100° to 600°, the resistance is an exponential function of the form $\log R = \log A + aT + Q/kT$. The specific resistance reaches a minimum at − 116° and again at 645°, the temperature coefficient changing from positive to negative with rising temperature. Its value at 0° is 0.089 ohm per cm. cube.

Periodic Relations among the Elements with Reference to Temperature Variation of Resistance are pointed out. High resistance elements toward the right side of the Periodic Table have characteristically negative coefficients while the good conductors toward the left side have positive coefficients. The elements in Group IV, C, Si, Ti, Ge and Zr show transitional behavior, each giving indications at least of a minimum resistance at temperatures which decrease regularly from very high for the lightest to very low for the heaviest element.

Transformation in Germanium, 125° to 450° C., as indicated by the above data, shows no hysteresis, the rapid cooling curves duplicating the slow cooling and heating ones. The phases are always in equilibrium, one, perhaps, being dissolved in the other.

THE production of a considerable quantity of pure metallic germanium under the direction of Professor L. M. Dennis, of the Department of Chemistry of Cornell University, has afforded an opportunity of studying the physical properties of this rare metal. Measurements of electrical resistance and thermo-electric power over a consider-

[1] The investigation upon which this article is based was supported by grants from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

able temperature range have been completed. The data are here shown graphically and discussed in connection with the position of germanium in the Periodic Table.

PREPARATION AND METHOD OF STUDY.

The germanium was originally prepared from chemically and spectroscopically pure germanium oxide by reduction with hydrogen in an electric furnace. The powdered metal was then fused under sodium sulphate and the solid mass obtained again powdered and boiled in dilute hydrochloric acid. It was then again melted in hydrogen. Very carefully taken spectra showed no lines except those of germanium. The sodium lines were especially looked for but were entirely absent. With the above treatment there is little likelihood that the metal contained oxide. This view is strengthened by the melting point determinations which gave 958.7° C. agreeing with the value previously found by Biltz[1] for oxide-free germanium. Biltz showed that with germanium containing small amounts of oxide a reduction of several degrees in the melting point occurred. His highest value for material treated as above and melted in hydrogen was 958 ± 5.0. Professor Dennis sets the purity as better than 99.9 per cent.

The specimen as received was in the form of a rod, 2.4 cm. long, 0.44 cm. wide, and 0.41 cm. thick. Junctions of platinum and platinum-10 per cent. rhodium were first placed in grooves filed into the bar near each end and were bound into tight contact with the germanium by means of fine platinum wire. The specimen was then placed between two small blocks of graphite which were held by springs tightly against the

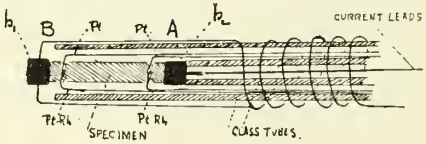


Fig. 1.

ends. Fig. 1 shows the arrangement. (b_1) and (b_2) are the graphite blocks through which current was led to the specimen. The block, (b_2), was pressed against the specimen by the glass tube through which one of the leading-in wires was passed. The block, (b_1), was pressed against the other end of the specimen by the tension of the other leading-in wire which was coiled as a spring around the glass tube, above mentioned, stretched and hooked into the far end of the tube. The leading-in wires were of nickel. The junction wires of platinum and platinum-

[1] W. Biltz, Zeit. f. Anorg. Chemie, 72, 313 (1911).

rhodium were led back along the tube, carefully insulated from one another and from the leading-in wires. The whole was enclosed in an outer glass tube. All the glass was pyrex.

Resistance was determined by sending current through the specimen, measuring the potential difference across the platinum wires as potential leads, and comparing the readings so obtained with the potential difference across a standard 1.0 ohm resistance placed in series. Measurements were made in this way in the following constant temperature baths: fresh liquid air (− 191° C.); old liquid air (oxygen) (− 183° C.); diethyl ether at its melting point (− 116° C.); carbon dioxide snow and ether (− 79° C.); freezing chloroform (− 65° C.); melting ice (0° C.); room temperature (+ 24° C.); and the following boiling points, chloroform (+ 61.2° C.), ethyl alcohol (77.5° C., with bar. at 736 mm.), water (98.9° C., with bar. at 732 mm.), anilin (183° C.), naphthalene (218° C.), benzophenone (305° C.) and sulphur (443° C., bar. 739 mm.). The temperature of the fresh liquid air was determined by extrapolation with a steel-constantan thermocouple, for the calibration of which liquid air four days old was taken as − 183° C. This temperature was indicated by a pentane thermometer originally calibrated by the Reichsanstalt. The resistance values obtained in the above baths are shown on the curve as points surrounded by circles. The specific resistance at zero Centigrade was found to be 0.089 ohm per cm. cube.

For thermo-electric power determinations it was necessary to establish a temperature gradient along the specimen, and then get the temperature at the point of contact of the platinum with the germanium near each end by means of the attached thermo-junction and to measure the electromotive force between the platinum leads when the specimen was on open circuit. The e.m.f. divided by the temperature difference gave the thermo-electric power for the mean temperature. For high-temperature determinations the specimen was placed in a vertical tubular furnace closed at the top with admission through the bottom. By adjusting the distance the specimen projected into the furnace any desired temperature gradient could be obtained. A heater coil of four turns of "chromel" wire wound on an asbestos tube and slipped over the specimen at *A* permitted of a reversal of the gradient when desired. Gradients varying from 5 to 60 degrees across the specimen were employed. Resistance measurements also were obtained under the same conditions. The large thermal e.m.f. was corrected for by reversing the current. The resistance values so obtained were assigned to the mean temperature and were found to fit exactly the curve obtained with constant temperature baths. Thus intermediate resistance points were obtained and likewise points beyond

the sulphur point as far as 675° C. It is to be noted that resistance values were obtained which may be regarded as simultaneous with the thermo-electric power data.

For data below room temperature, the platinum, platinum-rhodium couples were replaced by steel-constantan junctions, since the platinum couple is unsatisfactory for low temperature determinations, and the specimen was lowered into a long Dewar cylinder containing liquid air. Any temperature down to liquid-air temperature could be obtained sufficiently steady for satisfactory readings by merely adjusting the height of the specimen above the liquid air. By means of the heater coil the desired gradient could be maintained. The thermo-electric power against constantan was corrected to platinum.

The Thermo-Electric Power Line.

In the nature of the problem there always must be some uncertainty as to the actual temperature of the material at the point of contact with the junction wire. Exactly how closely the junction gives this temperature is open to question. It was originally hoped to thread the junction wires through very fine holes drilled through near each end. Germanium, however, is extremely hard and very brittle and no impression whatever could be made on the material with a drill. In spite of the uncertainty in respect to actual temperature the data certainly give the course of the thermo-electric power with fair accuracy. The thermo-electric power line shown represents the mean of several runs. Three runs were made using the heater coil which produced a thermal gradient down the specimen, *i.e.*, from A to B (Fig. 1), and two runs in which the heater coil was removed and a gradient established by the furnace in the opposite direction, *i.e.*, from B to A. The first three runs gave a curve which repeated itself very accurately. With the gradient reversed a slightly different curve was obtained which also was accurately repeated. Analysis of the conditions shows that the correct curve must lie between these two.[1] The line shown represents the most probable values of the thermo-electric power being the mean of the two sets of data.

[1] With the heat flow from A to B the junction at B must be heated from the specimen and therefore must be at slightly lower temperature than the specimen. If the heat flow is largely from the carbon block (b_2) into the specimen, the junction at A will also be at a lower temperature than the specimen. The heat flow at A was more nearly laterally inward since the heater coil was adjusted very nearly over the end of the specimen. The junction at A would thus be slightly warmer than the specimen. Thus the error at each end was in such a direction as to make the gradient appear larger than it actually was and to make the computed thermo-electric power too small. With the gradient in the other direction the heat reaches the specimen by way of the graphite block (b_1) and the junction at (B) is heated from the specimen. At (A) we have more nearly temperature equilibrium with the surroundings, therefore the discrepancy and between the temperature of the specimen that of the junction

The thermo-electric power line is straight from liquid-air temperatures up to about + 125° and again straight from 450° to 700°. Between these temperatures a transformation of some sort is shown by this line and also by the resistance curve. The transformation is a slow reversible one beginning at about + 125° and reaching completion at about 450°. Its completion apparently depends only upon the temperature and in no way upon the time. A careful study was made of this point as a result of a suggestion that if the changes were made more slowly the thermo-electric power line would be steeper in the transition region or if the temperature were held constant at some point in the transition region the change would progressively continue until all the material was in the second state. In this case the thermo-electric power line should

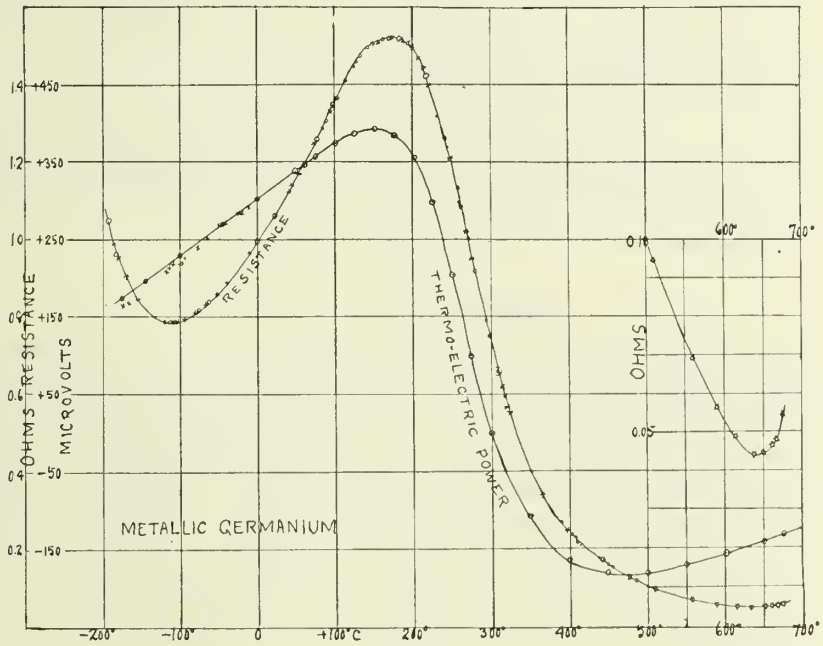


Fig. 2.

is not so great. The effect in this ease is to make the observed gradient too low and the computed thermo-electric power too great. The per cent. variation from the mean was found to depend upon the temperature gradient, the per eent. error being less with larger gradients. In the region of 100°–200° where the gradient maintained was about 10°–15°, the per eent. variation from the mean was as high as 7 per cent. Above 400° where a gradient of 35° or higher was maintained the variation of either set of values from the mean was about 2 per cent. Below room temperature thedirection of heat flow was always from *A* to *B*. Extremely low temperature data could only be obtained with small gradients of the order of 4 to 6 degrees. It is therefore to be expected that these values would be low and that the per cent. deviation would be greater than athigher temperatures where larger gradients eould be maintained.

drop vertically until it reached the line for the second state projected back. To test this point the specimen was held at a mean temperature of + 156° with a gradient of 12° for four hours. Absolutely no change in the thermo-electric power or resistance occurred throughout that time. The temperature was then raised to + 176° and held again for four hours. Again the thermo-electric power and resistance remained absolutely constant. A run was made very slowly through the entire transition region holding the temperature at each point constant for about three quarters of an hour. The points exactly checked the more rapid runs. The specimen was then cooled rapidly from 500° to points in the transition region with the idea of determining if the second state could be carried below 450° without the transition setting in. The rapid cooling curve exactly duplicated the slow heating one. The curves therefore appear to represent equilibrium conditions with a certain percentage of the second modification in solution in the first.

Up to 300° C. the thermo-electric power is positive with reference to platinum. It becomes zero at 300° and is negative above that temperature. The positive sign means that current flows across the hot junction from platinum to germanium or that in the external circuit the direction of flow is from germanium to platinum.

The Resistance Line.

From liquid-air temperature to + 100° C. the resistance of germanium follows a definite exponential law of the type $R = Ae^{[(Q/kT)+aT]}$, requiring a minimum at − 116° C. and a change in the temperature coefficient at that point from negative to positive. Above 600° the law is again found to hold but with different constants. In the intermediate region the law is entirely obscured by the transformation. Resistance minima were found at − 116° C. and + 645° C. The law is the same as that found by the writer to hold for iron oxide (Fe_2O_3) and was tested by a graphical method previously applied to that material.[1] This law is obtained by substituting for the empirical expression $R = R_0(1 + \alpha t + \beta t^2)$ the exponential form $R = R_0e^{aT}$, which holds equally well, and combining with this the expression $N = N_0e^{Q/kT}$ where N means the number of electrons taking part in electrical conduction. This latter expression was originally suggested by Königsberger[2] as representing the way the number of free electrons increases with temperature. Replacing R_0, by $Ae^{Q/kT}$ we have the law indicated above. A, Q, k and a are constant. Königsberger tested the law for several of the so-called non-metallic con-

[1] Bidwell, Phys. Rev., N. S., VIII., No. 1, 1916.

[2] Königsberger and Schilling, Ann. d. Phys., 32, 179, 1910.

ductors in the form $R = A(1 + \alpha t + \beta t^2)e^{Q/kT}$ by solving for the constants from known data and then checking computed values against observed ones. As has been shown the law in the modified form may be tested graphically by differentiating and writing the expression in the form

$$\frac{1}{R}\frac{dR}{dT} = \left(-\frac{Q}{k}\right)\frac{1}{T^2} + a.$$

dR/dT is the slope of the resistance line and may be measured. If the law is true we should get a straight line by plotting values of $(1/R\ dR/dT)$ as ordinates against values of $(1/T^2)$ as abscissa. The plot of this equation is shown, Fig. 3. It is apparent from this line that the law expresses

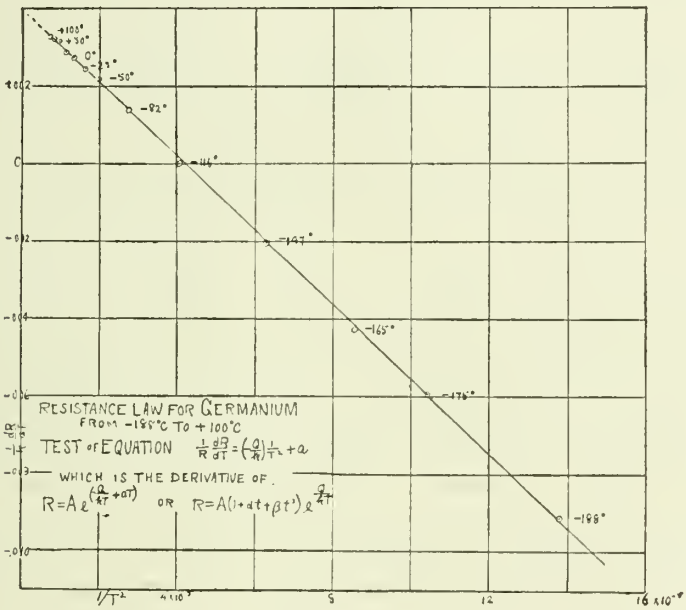


Fig. 3.

accurately the relation between resistance and temperature which is here followed.

Periodic Relations among the Elements with Reference to Temperature Variation of Resistance.

A reference to the Periodic Table and Group IV. to which germanium belongs is very instructive. Carbon, the first element in this group, appears to follow a similar law with a minimum at some very high temperature. Silicon, titanium and zirconium have been studied by

Königsberger[3] and found to follow the law. Silicon has a negative temperature coefficient with a minimum obscured by transformations but apparently not as high as that of carbon. Titanium shows a minimum at about + 100° C. Germanium now falls in line with a minimum at − 116° C. Zirconium and tin[1] show inflections at still lower temperatures indicating an approach to a minimum. It may be well to recall in this connection that the extremely high resistance elements which occur toward the right end of the Periodic Table have characteristically negative temperature coefficients, while the very good conductors which occur usually toward the left end have positive temperature coefficients of resistance.[2] The Group IV. elements which in respect to so many properties are the transitional elements, are in this sense also the transitional ones, for in this group the change from positive to negative temperature coefficient of resistance occurs at temperatures within reach and while the element is in the solid state. As the heavier elements are characteristically better conductors than the lighter ones the transition from positive to negative would be expected to occur for these farther to the right, or in the same group the transition from negative to positive coefficient would occur earlier, *i.e.*, at lower temperatures for the heavier elements. This is borne out by the behavior of the Group IV. elements as shown above. In Group V. a careful study will probably reveal similar behavior for phosphorus, arsenic, antimony and bismuth. In Group VI. only the very heaviest elements may be expected to still show a positive temperature coefficient. At low temperatures the coefficient is still positive for tellurium.[3] In Group III. only the lighter elements may be expected to still have a *negative* coefficient. Boron,[4] the lightest, shows a negative coefficient. The minimum for boron has not been reported but is indicated as occurring at a very high temperature. The minimum for aluminum may possibly be located at a very low temperature. It is possible that beryllium of Group II. may show the transition if studied through the low temperature ranges. This work is now being undertaken.

That a single law should cover the resistance changes for ger-

[1] Onnes and Holst, Leiden Com., 142 (*a*), 1914.

[2] The elements are usually classified in this respect as conductors of the first class (those with positive temperature coefficients) and conductors of the second class (those with negative coefficients). Electrolytes which characteristically have negative temperature coefficients are usually included in this classification. Electrolytic conduction, however, is an entirely different phenomenon, follows a different resistance law and shows the distinctive characteristic of polarization. Electrolytes are to be considered as forming a separate class with which we are not here concerned.

[3] Onnes, Leiden Com., 132 (*d*), 1912.

[4] Weintraub, Jour. Ind. Chem., Feb., 1913.

manium up to a temperature of + 100° is strengthened by the behavior of the thermo-electric line through this region. This curve indicates that there is nothing in the way of a molecular transformation occurring at − 116° where the resistance minimum is found. The thermo-electric power is extremely susceptible to molecular modifications and therefore indicates where the resistance law may be expected to hold and where it may be expected to be obscured by the occurrence of molecular changes.

Data on resistance and thermo-electric power for several other rare elements will be reported in a later paper.

Cornell University,
December, 1921.

MAGNETOSTRICTION WITH SMALL MAGNETIZING FIELDS.

By John R. Hobbie, Jr.

Synopsis.

Piezo-electric Method of Measuring Extremely Small Magnetostriction Effects.—In this method, suggested by Pupin, the wire to be studied is surrounded by a solenoid through which an alternating current of known strength and frequency is sent, and the vibrations set up in the wire are transmitted to a piezo-electric crystal and the resulting electric charge is amplified and measured. (1) For elongations down to 2×10^{-9} the wire was hung directly from a *quartz crystal.* To measure the charge produced by a given magnetizing current, an electromotive force of the same frequency and adjusted by means of a Pupin wave balance to the proper phase, was fed to the amplifier through a vacuum tube in parallel with the one connected to the crystal, and the potential was varied until the note produced by the crystal was balanced out. The force corresponding to a given charge was determined with the aid of a condenser, one plate of which was suspended from the crystal. (2) By using the torsion of a *Rochelle salt* crystal, the sensitiveness was extended to 2×10^{-11}, and (3) by tuning both the crystal and the wire to resonance with the frequency used, a sensitiveness of 3×10^{-12} was reached. The last two arrangements were calibrated in absolute units by comparison of the results with those obtained with quartz. The smallest change previously measured was about 10^{-8}.

Magnetostriction with Small Magnetizing Fields.—An *iron* wire containing 0.1 per cent. C, and a wire of *electrolytic nickel* were studied. In each case the curve for magnetostriction as a function of the field is nearly linear, but slightly concave downward, and apparently passes through the origin. For fields of 1, 0.05 and 0.002 gauss, the ratio of magnetostriction to field strength is respectively 3, 2.4 and 4×10^{-9} for iron, and 2, 1 and 3×10^{-9} for nickel. The probable error is from 7 to 10 per cent. *The effect of increasing the tension* is to decrease the elongation of both metals. A rod of *bismuth* 8 cm. long was tested in a field of 12 gauss using the resonance method, but gave a negative result, indicating that the effect is at least 10,000 times less than for iron.

Pupin Wave Balance for varying the Phase of an Alternating Electromotive Force is described.

Historical.

OBSERVATIONS on magnetostriction, that is, on the change in the length of a piece of iron when subjected to a magnetic field, were made by Joule[1] in 1847. In 1873 Mayer[2] made a series of careful measurements of the effect and obtained coefficients of elongation and contraction which ranged from 4.86×10^{-7} to 4.78×10^{-6}.

A very thorough study of magnetostriction was made by Bidwell[3]

[1] J. P. Joule, "On the Effects of Magnetostriction upon the Dimensions of Iron and Steel Bars," Phil. Mag., XXX., 1847, pp. 76, 225.

[2] A. M. Mayer, "On the Magnetic Elongation of Rods of Iron and Steel," Phil. Mag., XLVI., 1873, p. 177.

[3] Shelford Bidwell, "On the Changes produced in the Length of Rods of Iron, Steel, and Nickel," Proc. Roy. Soc., Vol. 38, 1885, p. 265; Vol. 40, 1886, pp. 109, 257; "On the Changes

in investigations extending from 1885 to 1890. An optical lever was used to measure the change in length, and he was able to detect a change of 10^{-7} times the length of his specimen with accuracy. The iron was found to increase in length with increasing magnetization up to a certain critical value, at which the maximum elongation was reached. Beyond the critical value, the elongation diminished, and a large magnetizing field produced contraction. Nickel contracted at first, and continued to contract, even with magnetizing forces far greater than those which produced the maximum elongation in iron. Tension decreased the elongation in iron, and increased the contraction.

Nagaoka[1] in 1894 examined the hysteresis effects attending magnetostriction. He used an optical lever and a micrometer microscope, and was able to detect changes in length of about 10^{-7} centimeters.

In 1898 Stevens[2] measured the change in length by observing the shift produced in interference bands. The smallest change that he was able to detect was 4×10^{-8} per unit length.

General Method.

The attention of these investigators was devoted to a study of magnetostriction with large fields. Their methods did not permit its study with small fields. The method of the present investigation permits of its study with very small fields, and was invented by Professor Pupin, of Columbia University.

An alternating current of approximately five hundred cycles was applied to a helix surrounding the specimen, a stretched iron wire. Since the elongation did not depend upon the direction of the magnetizing field, the wire vibrated with a frequency twice that of the current. A piezo-electric crystal, either quartz or Rochelle salt, was attached to one end of the vibrating wire, and an alternating electromotive force was developed on the tin foil coatings of the crystal by varying the tension of the wire. This electromotive force was increased by a three-stage amplifier to such an extent that it produced a note in a telephone receiver, and thus indicated the presence of vibrations in the wire. The amplitude of these vibrations was determined by balancing out the note with a known electromotive force of opposite phase to that developed on

produced by Magnetization in the Dimensions of Rings and Rods of Iron and of some other Metals," Proc. Roy. Soc., Vol. 43, 1888, p. 406; Phil. Trans., Vol. 179, 1888, p. 205; "On the Effect of Tension upon Magnetic Changes of Length in Wires of Iron, Nickel, and Cobalt," Proc. Roy. Soc., Vol. 47, 1890, p. 469.

[1] H. Nagaoka, "Hysteresis attending the Change of Length by Magnetostriction in Nickel and Iron," Phil. Mag., XXXVII., 1894, p. 131.

[2] J. S. Stevens, "An Application of Interference Methods to a Study of the Changes Produced in Metals by Magnetization," Phys. Rev., Vol. 7, 1898, p. 19.

the crystal. As the crystal had been calibrated by determining the potentials required to balance tensions of various amplitudes, the amplitude of the vibrations in the wire could be calculated.

With the larger magnetizing fields a quartz crystal was used. The specimen hung from the crystal, as shown in Fig. 1, and the helix through which the magnetizing current passed was wound directly on the wire. Approximately half the length of the wire was wound in this manner.

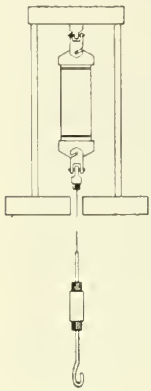


Fig. 1.

Method of suspending quartz crystal and wire.

If it is assumed that the rigidity of the crystal and its supports was large compared to that of the wire, and that the mass suspended from the wire was large compared to the mass of the wire, we can write, owing to the large frequency and large suspended mass used,

$$K = -Fl/l's Y, \tag{1}$$

where K is the amplitude of elongation per unit length due to a given magnetizing field, F the amplitude of the variation in tension due to the elongation, l the total length of the wire, l' the length of the magnetized portion, s the cross section, and Y Young's modulus for the wire.

That which was measured directly was not F but the virtual electromotive force, E, developed on the crystal. A determination of the relation between E and F was necessary.

To effect this, one plate of a parallel plate condenser hung from the quartz crystal, and the other plate was placed just below it on a board which could be raised or lowered by levelling screws. Suppose now that a known electromotive force of the same frequency as that applied to the helix is applied to the condenser. The force of attraction of the lower plate upon the upper one is easily calculated and the electromotive force developed on the crystal found in terms of the mechanical force acting on it.

The attractive force is given by the equation,

$$F_0 = A V^2(10^{-4})/72\pi d^2, \tag{2}$$

where F_0 is the virtual attractive force between the condenser plates, A the area of the plates, V the virtual electromotive force applied to the condenser, and d the distance between the plates of the condenser.

If we write, for the relation between the tension produced on the crystal and the electromotive force developed by it, $F_0 = Ez$, we have, since the attractive force F_0 is related to the amplitude F of the tension

producing a virtual electromotive force E on the crystal by the equation,

$$F = \sqrt{2}\, F_0,$$

$$F = \sqrt{2}\, Ez, \quad \text{or} \quad K = -\sqrt{2}\, Ezl/l'sY = \sqrt{2}\, EzD. \tag{3}$$

The balancing electromotive force, of the same frequency as that developed by the crystal, was obtained by applying the magnetizing current to the grid of a vacuum tube. The arrangement is shown in Fig. 2. The magnetizing current, obtained from an alternating current machine giving a pure sine wave of 535 cycles, was applied to the grid of the tube T_1. A resistance between the grid of this tube and ground maintained the grid at a negative potential with respect to the filament, and the resulting distortion of the plate current gave rise to a series of overtones. The fundamental and all overtones except the first were short-circuited by a circuit TC 1, tuned to resonance at 1,070 cycles. The current of double frequency thus obtained was increased by a power tube T_2.

An electrostatic voltmeter V was used to measure the voltage, and a potentiometer P_1 to take off the amount needed for balancing.

The phase of the balancing electromotive force was regulated so as to be opposite to that produced by the crystal by a wave balance, WB, developed by Professor Pupin. It consists of a number of coils in series, with a condenser between each pair of coils and ground. These coils, which constitute the primary, are wound on a single tube in such a way that a secondary coil fitting over the tube can be moved along it. When an alternating electromotive force is applied to the first coil it is transmitted along the coils with a varying phase and a continuously diminishing amplitude. The attenuation has such a value that no stationary wave effects due to reflection at the end of the wave balance are appreciable. An electromotive force is induced in the secondary, the phase and amplitude of which depend upon its position on the primary coil.

In the particular wave balance used, the size and number of coils and condensers were such that there was a change of phase of about two hundred degrees from one end of the primary coil to the other. Thus, with the aid of a reversing switch S_2 in the secondary circuit, an electromotive force of any desired phase could be obtained for balancing.

To balance the electromotive force from the crystal and from the wave balance two repeating tubes, T_3 and T_4, Fig. 2, were connected in parallel as shown. The amplification ratio, A, of the two tubes was determined by sending to the grid of T_4, through a potentiometer P_2–P_3, and a two-way switch S_3, the same current that was supplied to thew ave-balance and its tube.

A test of the constancy of this ratio for various settings of potentiometer 3 was made, and the average variation from the mean found to be only about one per cent.

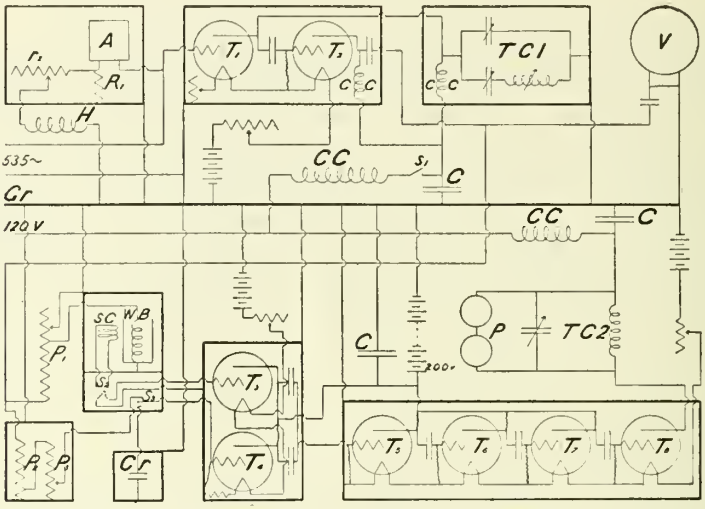


Fig. 2.

Diagram of electrical apparatus.

Equation (3) can now be written in the form

$$K = \sqrt{2}\, DzAP_1WV, \tag{4}$$

where P_1 is the ratio of potentiometer 1, W the ratio of the wave balance, and V the voltage applied to potentiometer 1.

The combined current from the two repeating tubes passed through a three-stage amplifier, made up of tubes T_5, T_6, T_7, the plates of which were fed from a two hundred volt dry battery. T_8 was a power tube used to supply the current to actuate the telephones P. A circuit TC 2 was adjusted to resonance for the frequency of the note which was to be heard in the telephones.

Complete electrical shielding was found necessary to prevent the amplifier from picking up stray oscillations which interfered with the balancing. This shielding is indicated in the figure by heavy lines. All parts of the circuit were grounded radially to the heavy ground wire, Gr.

The magnetizing helix surrounding the iron wire is shown at H. It was fed from the alternator through an ammeter A and a variable resistance r_2, which regulated the current flowing in the helix, in shunt with R_1. The amplitude of the magnetizing force is given by

$$H = 4\pi nI\sqrt{2}/10, \tag{5}$$

where n is the number of turns of wire per centimeter in the helix. The factor $\sqrt{2}$ is introduced since I, as determined from the ammeter reading, is the virtual current.

The coils CC were choke coils of sufficient impedance to prevent commutation from the one hundred and twenty volt machine entering different parts of the circuit, and to prevent oscillations set up at one point from reaching a point where they were not desired. The condensers C served the same purpose by furnishing a ground for any current which might get by the choke coils.

Use of Rochelle Salt.

Below one gauss, the results with quartz were not dependable, so Rochelle salt was used for the lower fields. The absolute value of K could not be calculated with the Rochelle salt, but the shape of the curve could be determined, and matched up with the curve obtained by the quartz for the same region, thus getting the value of K indirectly.

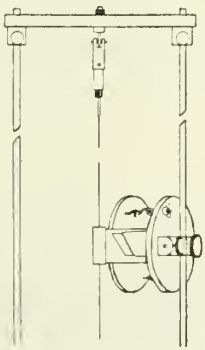


Fig. 3.

Method of supporting Rochelle salt crystal and wire.

The Rochelle salt crystal used was obtained through the kindness of Dr. A. M. Nicolson of the Western Electric Company. The mounting was the same as he had used in a phonograph transmitter,[1] and the method of attaching it to the wire is shown in Fig. 3. The iron wire hung from a brass block, the vibration of which was communicated to the crystal. The block was supported by a brass wire. In this way the weights suspended from the iron wire were supported by the brass wire and produced no strain on the crystal, but the elasticity of the brass wire permitted the vibrations due to the magnetostriction to be transmitted to the crystal. The vibration produced in the crystal was a torsional one, to which the crystal was most sensitive.

Resonance Method.

To increase the sensitiveness of the method still more, Professor Pupin suggested using a wire and a crystal resonant to the frequency of the impressed vibrations.

A Rochelle salt crystal which, with its mounting, had a natural frequency between 1,050 and 1,100 vibrations per second was used in connection with a wire which had a length of one wave-length for longi-

[1] A. McL. Nicolson, "The Piezo-Electric Effect in the Composite Rochelle Salt Crystal," Proc. Am. I. E. E., Vol. 38, p. 1315, Nov., 1919.

tudinal vibrations of this frequency. The resonant crystal was furnished by Dr. Nicolson.

This wire was stretched in a horizontal position and held tightly by passing over a pulley and hanging weights from the end. Connection between the wire and the crystal was made in such a manner that the crystal could be moved back and forth from the end of the wire until a point was found where the note was of maximum intensity.

The alternator previously used was replaced by an oscillator, so that the frequency could be varied over a small range. To tune the circuit, the length of the wire was changed by moving a stop at its far end until a note of maximum intensity was produced when the oscillator was adjusted to a frequency corresponding to the length of the wire. This was taken to be the resonant frequency of the crystal.

Calculation of the absolute value of K could not be made directly, so the shape of the curve was obtained, and the ordinates multiplied by the proper constant to make them fit the previous curves.

Method of Experimentation.

For any run with the quartz crystal the switch S_3, Fig. 2, was thrown so as to connect the grid of T_4 with the potentiometer 3, and the note produced by the current from potentiometers 2 and 3 was balanced out by adjusting potentiometer 1 and the wave balance. This balance was made by setting the potentiometer and wave balance alternately for minimum sound in the telephone, until no sound was heard.

After measuring the amplification ratio, the crystal was connected to the grid of T_4, and a run was made by balancing out the note produced by the crystal under varying conditions.

Results with Quartz.

Runs with the quartz crystal were made with an iron wire containing about one tenth of one per cent. of carbon, and with a wire of electrolytic nickel. Both the iron and the nickel wires were stretched to remove kinks, then annealed by heating to a red heat.

The smallest weights used were found to be necessary to keep the wire stretched; the largest weights were about as much as could be used without producing a permanent stretch in the wire. The mean results of several runs under different conditions are shown in Figs. 4, 5, and 6.

The general character of the effect agrees with that which Bidwell obtained for small fields. The fact that a contraction is obtained in the case of nickel does not appear from the present method, which measures only the magnitude of the change, but does not indicate whether it is an elongation or a contraction.

The precision of the results shown in these curves is from seven to ten per cent.

The results with quartz correspond to those of Bidwell. This, together with the fact that a brass wire in place of the iron gave no sound, shows

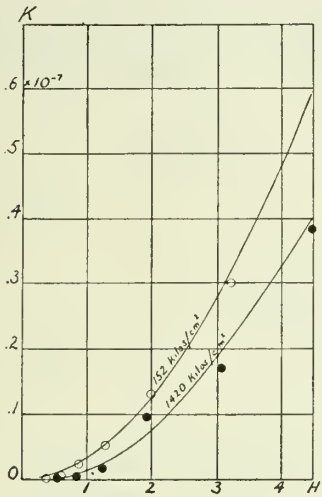


Fig. 4.

Amplitude of elongation per unit length vs. amplitude of magnetizing field (gauss). Low and high tensions. Quartz crystal. Iron wire.

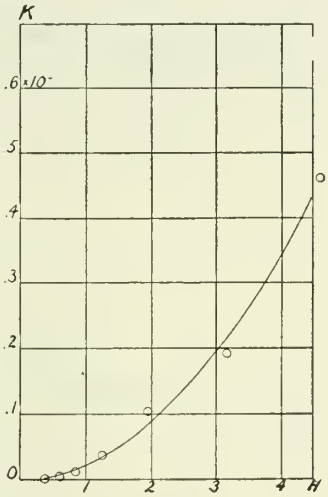


Fig. 5.

Amplitude of elongation per unit length vs. amplitude of magnetizing field (gauss). Low tension. Quartz crystal. Nickel wire.

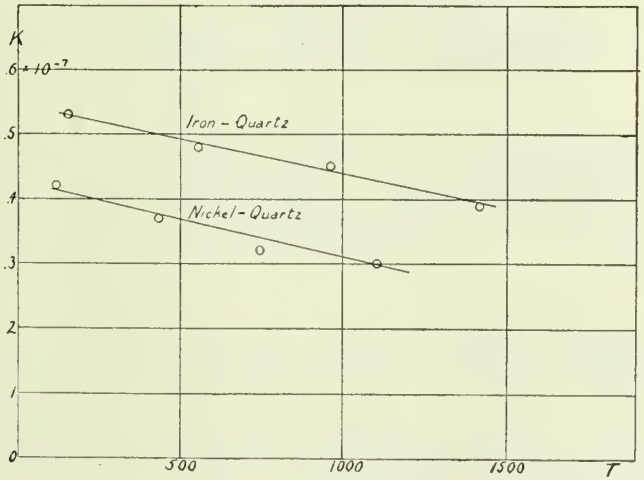


Fig. 6.

Amplitude of elongation per unit length vs. tension in wire (kgms./cm.²). Quartz crystal. Iron and Nickel Wires.

that the effect is due to magnetostriction, rather than to any direct magnetic effect of the helix.

RESULTS WITH ROCHELLE SALT.

The results with quartz were most dependable above one gauss. The Rochelle salt gave curves that checked with those of quartz if the magnitude of the field was not greater than two gauss. For this reason

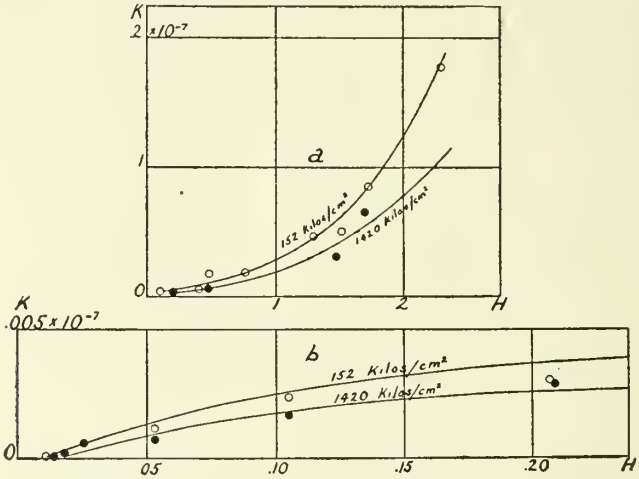


Fig. 7.

Amplitude of elongation per unit length vs. amplitude of magnetizing field (gauss). Low and high tensions. Rochelle salt crystal. Iron wire.

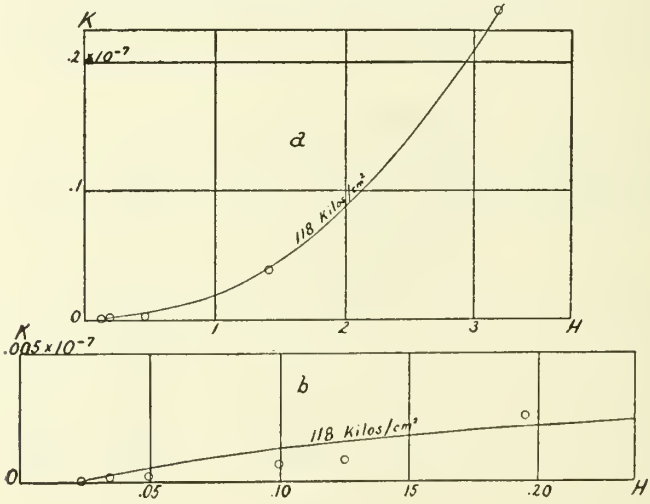


Fig. 8.

Amplitude of elongation per unit length vs. amplitude of magnetizing field (gauss). Low tension. Rochelle salt crystal. Nickel wire.

the multiplying factor applied to the Rochelle salt values was such as to make them fit the quartz curve most closely between one and two gauss.

The results are plotted in Figs. 7 *a* and *b*, and 8 *a* and *b*. The larger scales show the lower portions of the curves. A blank run with a brass wire gave no effect.

With the resonant wire and crystal the greatest effect was obtained when the tension in the wire was greatest, so the runs were made with the maximum tension, 1420 kilos per square centimeter, previously used. The results with the iron wire are plotted in Fig. 9 *a*, *b*, *c*, on successively

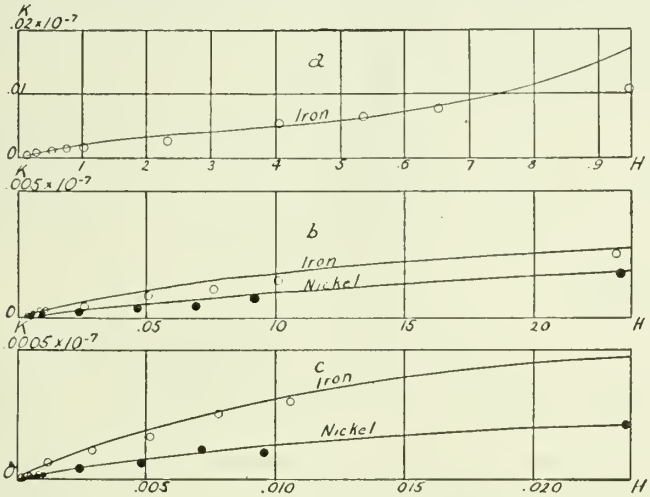


Fig. 9.

Amplitude of elongation per unit length vs. amplitude of magnetizing field (gauss). Resonant wire and crystal. Iron and Nickel Wires.

larger scales. Comparison of Figs. 7*a* and 9*a* shows that the resonant curve fits the previous one for values of H less than 0.6 gauss. Above this value the resonant curve is less, doubtless due to excessive damping in the case of the vibrations of greater amplitude. The curves shown in Fig. 9 *b* and *c* are more dependable than those in Fig. 7*b* for the lower portion of the curve.

Runs were made with the nickel wire in the same manner as with the iron, except that a tension of 747 kilos per square centimeter was used. The results are shown in Fig. 9 *b* and *c*. Since no run with the quartz crystal and nickel wire was made at this tension, the curves for nickel in Fig. 9 *b* and *c* can only be regarded as a rough approximation to the absolute value. Their shape, however, can be depended on.

By means of the resonant method the curve has been extended to 0.002 of a gauss in the case of iron, and to 0.005 of a gauss in the case of

nickel. At these values the effect could just be detected. A brass wire substituted for the iron or nickel produced no effect.

In each case the shape of the curve was the same; that is, nearly linear but slightly concave downward in its lower portion, apparently passing through the origin.

EXPERIMENTS WITH BISMUTH.

In the account of Bidwell's work[1] he tells of detecting magnetostriction in bismuth. The effect was small but measurable. Later Wills[2] undertook to measure the effect. Using specially prepared very pure bismuth and an apparatus which would have detected a change of 10^{-8} times the length of the specimen, one centimeter, he was unable to observe any effect with a field as high as 3,200 gauss.

If Bidwell's results were correct, a field of seven gauss should give an elongation great enough to come within the limits of the resonant method, about 3×10^{-12}. A rod of bismuth about eight centimeters long and one half a centimeter in diameter was wound with a helix to within about one centimeter of each end, and attached to a brass wire of the resonant length.

The power of the amplifier was increased, and a field of twelve gauss applied to the bismuth, but without producing any effect. It would seem, then, that magnetostriction is lacking in bismuth, at least in fields of twelve gauss.

The writer wishes to express his obligations to Professors Pupin and Wills for frequent suggestions made during the development of the method and the progress of the investigation, and to the Western Electric Company and Dr. Nicolson for their kindness in furnishing the crystals of Rochelle salt, and in giving suggestions as to their use.

MARCELLUS HARTLEY RESEARCH LABORATORY,
COLUMBIA UNIVERSITY,
August, 1921.

[1] Shelford Bidwell, "On the Changes Produced by Magnetization in the Dimensions of Rings and Rods of Iron and of Some other Metals," Phil. Trans., Vol. 179, 1888, p. 205.

[2] A. P. Wills, "On Magnetostriction in Bismuth," PHYS. REV., Vol. 15, 1902, p. 1.

A NOTE ON THE PRESSURE OF RADIATION ON TRANSPARENT DIELECTRICS.

By Satyendra Ray.

Synopsis.

Suggested Explanation of Photophoresis, that is the attraction or repulsion of microscopic particles by light as observed by Ehrenhaft and others. It has previously been shown that there are electric and magnetic forces acting on an illuminated transparent body in the direction of propagation of the light if the ether has an electric density (Pe) and a magnetic density (Pm) other than zero. When one dielectric is immersed in another, the difference between these radiation forces per unit volume acting on the two media, would give rise to a relative motion which may be either in the direction of the light or in the opposite direction.

A Quantum Relation in Maxwell's Electromagnetic Theory is obtained if we equate the radiation pressure per unit area in terms of Pe and Pm to the pressure derived from the stresses assumed by Maxwell to exist in electric and magnetic tubes of force, namely, the ratio of the amplitude to the wave-length of light is a constant.

THE phenomenon of "negative photophoresis" discovered by Ehrenhaft requires a reëxamination of our notion of radiation pressure. The most serious difficulty in the way of a radiometric interpretation of the phenomenon as given by Westphal and Gerlach, Rubinowicz, Laski and Zerner, etc., is the doubt it throws on the experiments of Lebedew, and Nichols and Hull as having established this radiation pressure. Millikan points out how the droplet suspended in his condenser by the proper electrical field forms an electrical balance that "will weigh accurately and easily to one ten-billionth part of a milligram." Ehrenhaft's condenser using (1) much smaller particles and (2) a microscope in place of a telescope for observations, is quite a thousand times more sensitive. Again, as Ehrenhaft points out (Ann. d. Phys., 56, p. 83) for spherical particles radiation pressure is proportional to the square of the radius while its mass is proportional to its cube so that the acceleration effect would be inversely proportional to the radius and becomes infinitely great for infinitely small values of r. If then under such highly favorable conditions, theoretical as well as experimental, we find the "photophoretic force" almost as often as not [1] negative in character and if to

[1] An interesting relation between the photophoretic character of an element and its position in the periodic table is given by Mattauch in the following words, "Wie F. Ehrenhaft in einem Vortrage über die Photophorese in der chem.-phys. Ges. in Wien (März, 1919) erwähnte, erweisen sich, soweit die Materialien bisher von ihm und seinen Schülern untersucht sind, Na, K, Cu, Ag, Au, ferner Mg, Zn, Cd und Hg, also die Elemente der Kolonnen I und II des periodischen Systems als lichtpositiv. Lichtnegativ dagegen sind S, P, Sn, Pb und Te, also die Elemente der Kolonnen III und IV und ebenso der Kolonnen V bis VII. Die den letz-

explain the negative sign we are thrown back upon a radiometric explanation, all experiments hitherto done to experimentally establish radiation pressure are naturally discredited.

In this connection attention is invited to a paper by Michaud, who, in order to explain negative photophoresis, showed from thermodynamic considerations the possibility of light pull instead of light pressure for *transparent* substances.[1]

In the radiometric interpretation of negative photophoresis it is assumed that it is impossible to explain it on the electromagnetic theory of light.[2] It would be interesting to examine the *steady* forces in the beam of light mentioned in the note on the plane wave[3] for an explanation of negative photophoresis.

The constant intensities in the direction of propagation of a plane wave lead us to a simple expression for the pressure of radiation on transparent bodies. The constant intensities $2\rho_e\Lambda/K$ and $2\rho_m\Lambda/\mu$ give us, by definition, forces acting per unit charge in a direction parallel to that of propagation. The forces per unit volume would be $2\rho_e^2\Lambda/K$ and $2\rho_m^2\Lambda/\mu$ respectively. The mechanical force per unit volume would be the sum of these two forces

$$F = \left(\frac{2\rho_e^2\Lambda}{K} + \frac{2\rho_m^2\Lambda}{\mu}\right).$$

The pressure in the usual form of force per unit area may be derived from the expression

$$F = \tfrac{1}{2}R\cdot N,$$

where

$$R = \frac{4\pi}{K}\cdot N.$$

Substituting for R the value $2\rho_e\Lambda/K$ we have, therefore, due to the electric force,

$$F_1 = \frac{\rho_e^2\Lambda^2}{2\pi K}.$$

Similarly, due to the magnetic force,

$$F_2 = \frac{\rho_m^2\Lambda^2}{2\pi\mu}.$$

teren Kolonnen angehörenden Elemente As, Se, Sb, Te und J, die in verschiedenen allotropen Modifikationen auftreten, haben aber, wie dortselbst auseinandergesetzt wurde, noch die besondere Eigenschaft dass bei ihrer Verdampfung sowohl lichtpositive als auch lichtnegative Probekörper entstehen." Neue Versuche zur Photophorese, Sitzungsber. d. Wien. Akad. d. Wiss., 129 (IIa), 1920.

[1] C. R., Vol. 168, Nr. 15, 14 April, 1919.

[2] Zerner and Laski in Zeit. f. Physik., March 4, 1920, p. 226.

[3] PHYS. REV., Nov., 1921.

And the resultant force,

$$F = \frac{\Lambda^2}{2\pi}\left(\frac{\rho_e^2}{K} + \frac{\rho_m^2}{\mu}\right). \tag{1}$$

We notice the expression on the right-hand side is of the dimensions of a pressure, and that it is, apparently, independent of the amplitude of vibration in the light disturbance. Maxwell's conception of stresses in the electric and magnetic tubes of force gives us another expression for the pressure, namely $KR^2/8\pi$. Obviously the two expressions are not independent of one another. They are either equal or bear a constant ratio to one another. We have

$$\frac{\rho_e^2\Lambda^2}{2\pi K} = \frac{c \cdot KR^2}{8\pi}$$

or

$$\frac{R^2}{\Lambda^2} = \frac{1}{c} \cdot \frac{4\rho_e^2}{K^2} = \text{constant}.$$

In words; the ratio between the amplitude and wave-length of light is constant. This interesting relation leads us to a quantum relation in Maxwell's electromagnetic theory and makes the law of equipartition of energy satisfied in the light-wave through ether.

Equation (1) gives us a steady pressure instead of the average of a variable effect and is obtained directly from the fundamental equations. The magnitude of this constant force will depend upon the dielectric. In the case of one dielectric being immersed in another the difference in magnitude of force per unit volume will cause a relative motion parallel to the direction of propagation. The sense of motion, however, can as easily be towards the source of light as away from it. A particle immersed in a fluid gives us a gravitational analogue. The earth's pull exerts a downward force on the particle immersed as well as on each element of the fluid. Whether the particle would rise or sink depends upon whether its gravitational density is smaller or greater than that of the fluid. In this analogy "negative photophoresis" corresponds to buoyancy.

In connection with the "electric density" of dielectrics attention may be directed to an aspect of modern atomic theories. They are not neutral.[1] The necessary excess of charge gives us an electric density.

[1] Broughall, Phil. Mag., Vol. 41, p. 872.

University College, London,
December 16, 1921.

THE ELECTRODELESS DISCHARGE IN CERTAIN VAPORS.

By J. K. Robertson.

Synopsis.

Appearance and Spectrum of Electrodeless Discharge in Various Vapors.—The discharge was produced by electromagnetic induction, the bulbs containing the vapors being placed within a Tesla coil through which passed a high-frequency condenser discharge. The effect was found to *vary with vapor pressure*, controlled by the temperature, *and with electromotive force*, controlled by a spark gap. In general, for a certain range of pressure, an intense ring discharge was obtained which weakened to a faint luminosity for higher pressures. *Potassium* at temperatures of 250–300° C., gave a bright ring with a spectrum including seven or more members of each subordinate series. The bright yellow discharge in *sodium* above 300° C. showed the *D*-lines, four members of the diffuse series and three members of the sharp series. With *lithium* up to 500° C. only a feeble discharge due to impurities was obtained. In the case of *mercury*, the work of Kowalski was confirmed and extended. A dazzling white ring discharge appeared from 70 to 110° C. or higher depending on the spark gap; then became fainter, while a greenish glow whose spectrum showed a few lines superposed on a continuous band extending from the violet to the yellow, appeared for 110 to 115° C., *irrespective of the spark gap.* It is suggested that the glow may be associated with polyatomic molecules formed at the higher vapor pressures. In the case of *iodine*, the only diatomic vapor studied, at temperatures from − 5° to 5° C. a pale yellow ring showing a band spectrum changed to a green, pink-bordered ring with a line spectrum when the spark gap was increased; the higher the pressure, the greater the spark length necessary to excite the line spectrum. The change probably accompanies dissociation of the molecules into atoms.

Electrodeless Discharge as a Source of Sharp Lines should be of value in measuring wave-lengths and in analyzing, with an instrument of high dispersion, lines with components due to isotopes.

ALTHOUGH the subject of investigation by Sir J. J. Thomson as long ago as 1892, the electrodeless discharge has been utilized but little by spectroscopists. Some time ago it occurred to the writer that it might be worth while to try to obtain this type of discharge in the case of the more easily vaporized metals. Because of the comparatively simple conditions of discharge, combined with the absence of electrodes and the ease with which ordinary impurities can be avoided, it was thought that much valuable information might be gained from such a spectroscopic study. Circumstances have not made possible as yet an exhaustive investigation, but enough has been done to show that this type of discharge provides a most useful source for the study not only of the vacuum arc spectrum of such metals as sodium and potassium, but also, as in the case of the diatomic vapor of iodine, of the change in the spectrum brought about by dissociation. Since the investigation was

undertaken, it has been noted that McLennan[1] made use of this type of discharge in his work on the spectral series of mercury, while Kowalski[2] examined the change in the appearance of the discharge in the same vapor with changing temperature. Hagenbach and Frey,[3] moreover, have made a preliminary report of a spectroscopic study of the discharge in many gases and vapors. It will be seen below, however, that these writers, in the case of sodium and of iodine, failed to obtain the proper discharge. Quite recently Dunoyer[4] has published a report on the spectrum of cæsium, obtained also from the discharge excited by electromagnetic induction.

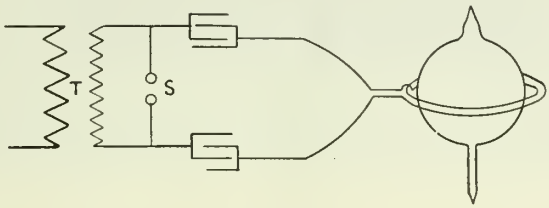


Fig. 1.

The experimental arrangement differed little from that first used by Sir J. J. Thomson. A bulb, some 12 cm. in diameter was suspended inside a coil of six co-planar turns of stout copper wire through which passed the high-frequency oscillatory discharge of two Leyden jars connected as shown in the diagram (capacity of each $5\text{–}7 \times 10^2$ absolute electrostatic units). A clearance of some two to four millimeters existed between the outside of the bulb and the innermost turn of the coil. The jars were charged in some cases by an induction coil but subsequently by means of a small interrupterless x-ray transformer T, while the spark gap S enabled one to control the intensity of the exciting field inside the bulb. It may be noted here that Bergen Davis[5] has shown that the mean value of the electrical intensity inside the bulb is directly proportional to the potential at the spark gap.

By means of a Langmuir condensation pump with auxiliary, the bulbs of pyrex glass were exhausted to a pressure of the order of 0.0002 mm. Hg., he flame of a large Meker burner being played over each of them for an hour during exhaustion. The vapor o' the element to be used was then distilled over from a side tube, and the bulb finally sealed off both from the side arm and from the pumps. In the case of sodium,

[1] J. C. McLennan, Proc. Roy. Soc., A, 87, p. 256.

[2] J. Kowalski, Phys. Zeit., XV., No. 5, p. 249.

[3] Hagenbach and Frey, Phys. Zeit., XVIII., p. 544, 1917.

[4] M. L. Dunoyer, Comptes Rendus, Tome 175, No. 6, p. 350.

[5] Bergen Davis, Phys. Rev., Vol. XX., p. 129, 1905.

before sealing off from the pumps, the metal was "chased" about the bulb a number of times to drive off as much as possible occluded hydrogen.[1] The bulb to be used was then suspended within the primary coil, which in all cases so far studied except iodine, was inside an electric oven. In this way vapor pressures corresponding to temperatures as high as 500° C. could be obtained if necessary.

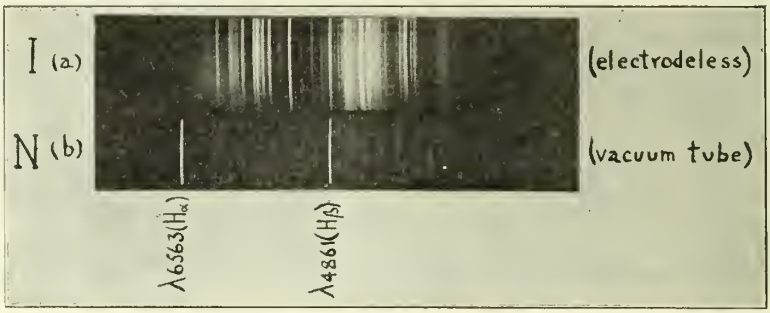


Fig. 2.

IODINE.

To obtain the discharge in iodine a projecting stem of the bulb was immersed in a vessel containing melting ice. It was found that two distinct types of ring discharge could be obtained. With a spark gap of the order of 1 mm., the ring had a pale yellow appearance, probably the same color as the chamois yellow which Wood[2] describes. Examination with a spectroscope of small dispersion showed a continuous band extending from red to green, then a wide absorption band, followed by a second apparently continuous band in the blue-violet. As the spark gap was increased in length, the appearance of the ring changed abruptly to a pale green ring with an inner pink border, the latter extending to a slightly greater distance above the plane of the coil than the green luminescence. The spectrum of this second type of discharge showed numerous bright lines, with faint continuous background in the red region. Photograph *a* in the accompanying plate is a photograph of the spectrum of the "green" discharge, made with a Hilger constant deviation spectrograph. The abrupt change in the appearance of the discharge is doubtless the result of dissociation, the pink border probably corresponding to the lesser degree of dissociation one might expect in the weaker electric field nearer the center of the bulb. It was at first thought that the pink luminosity might be due to nitrogen present as an impurity,

[1] R. W. Wood, Researches in Physical Optics, Part II., p. 178, 1919.

[2] R. W. Wood, Researches in Physical Optics, Part II., p. 53, 1919.

Wood [1] having observed that color in insufficiently exhausted iodine vacuum tubes. It will be seen from the plate, however, that there is no trace of nitrogen as far as one can judge from *b*, the comparison spectrum

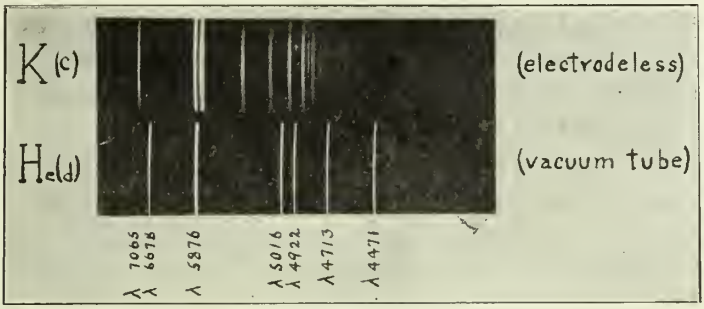


Fig. 3.

of a nitrogen vacuum tube (with hydrogen impurity). Observation with a small direct-vision spectroscope directed successively at the green and the pink portions of the ring showed that the lines in the pink were much feebler than in the green. This is what one would expect from a smaller degree of dissociation.

By varying the temperature of the bath in which the stem was immersed, it was shown that both types of ring discharge could be obtained at vapor pressures corresponding to temperatures lower than $-5°$ C. and higher than $+5°$ C. With increasing pressure, a longer gap was required to bring out the line discharge. This again is just what one would expect, because the higher the pressure, the shorter the free path of an electron or ion and so the greater the electric intensity necessary to give the electron the energy required to bring out the line spectrum.

As the pressure rises higher and higher, a stage is reached at which the discharge is accompanied by a general and comparatively feeble luminosity filling part or all of the bulb. It is not surprising that Hagenbach and Frey, who apparently worked with iodine only at room temperature, found the discharge in this case not brilliant.[2]

By slowly changing the spark gap, an attempt was made to see which line, if any, first became visible during the transition from the band to the line spectrum. A line approximately λ 4860 seemed to flash in first, although others followed so quickly that it was difficult to determine this conclusively. In this connection it is interesting to note that, if we apply the quantum relation, $eV = h\nu$, λ 4860 corresponds to a radiating poten-

[1] Researches in Physical Optics, Part II., p. 53, 1919.

[2] "Doch bildet sich die Ringentladung . . . nicht schön aus."—Hagenbach and Frey, loc. cit.

tial of 2.54 volts, while the value obtained for the resonance potential of iodine by direct experiment by Mohler and Foote[1] is 2.34 ± .2 volts. Moreover, Smyth and Compton,[2] in their work on the ionization of fluorescing iodine vapor, obtained 2.6 volts as a rough value for the quantum of absorbed radiant energy. This agreement, however, is probably purely accidental. Working with hydrogen, Franck[3] has shown that, in order to bring out the complete line spectrum, a voltage must be applied which is greater than the ionizing potential by an amount equal to the work of dissociation. It is probable, therefore, that in all diatomic gases the simple quantum relation cannot be applied without correction.

POTASSIUM.

At temperatures ranging from 250° to 300° C. no difficulty was experienced in obtaining a bright ring discharge in the case of potassium. The ring which is not so sharply defined as in the case of iodine, consists of a pale green portion, with an outer border of orange yellow. If the electrical intensity is great enough, a distinctly violet region is seen next the bulb. The spectrum shows the ordinary arc lines, as will be seen from photograph *c* in Fig. 3 where *d* is a comparison spectrum of helium. It was not possible with the small dispersion of the spectroscope to make any exact measurements of wave-lengths. Lines of the first and second subordinate series as far as λ 4805 were easily identified. Then followed a group of two or three faint lines, then λ 4757 (rough setting), then a group of seven or eight or more, until λ 4643 was read. This last is no doubt the combination pair 4642.17 and 4641.58 recently observed by Datta.[4] Further in the violet region lines were observed at values approximately λ 4607, λ 4506, λ 4390 and λ 4314. It would seem, therefore, that with this source one may obtain if anything higher members of the subordinate series than those measured by Datta.[5]

The sodium D lines always came out strongly, and at times the red sodium lines at λ 6161 were faintly visible. A few unidentified lines were visible, for the most part very faintly, although one at λ 5007 and another at λ 4831 were at times moderately intense.

As his source of light Datta used a potassium vapor lamp, similar in construction to the sodium lamp devised by Lord Rayleigh,[6] but much more troublesome to operate than the sodium. With the electrodeless

[1] Mohler and Foote, PHYS. REV., Vol. XV., No. 4, p. 321, 1920.

[2] H. D. Smyth and K. T. Compton, PHYS. REV., Vol. XVI., p. 501, 1920.

[3] J. Franck, Phys. Zeit., XXII., p. 468, 1921.

[4] S. Datta, Proc. Roy. Soc., A, 99, April, 1921.

[5] S. Datta, loc. cit.

[6] R. J. Strutt, Proc. Roy. Soc., A, 96, p. 272, 1919.

arra ngement no difficulty whatever was experienced, and it was found that observations could be extended over a series of days. Indeed, a bulb which has been used on four or five different occasions, is only slightly discolored and may still be used for further observations.

Such a source, moreover, because of the low vapor pressure at which the luminous discharge occurs, should be suitable for a study of the structure of single lines. If potassium is a mixture of two isotopes, as recently shown by Aston, one might expect each line of a doublet to be made up of two components. It might be well worth while, therefore, to examine the structure of some of the potassium lines from the above source with a sufficiently high resolving power. Making use of the difference in wave-lengths obtained by Merton[1] for different specimens of lead (0.002 Å.u.–0.005 Å.u.) one might expect for potassium lines a separation of possible components approximately (0.002–0.005) × 207/40 or (0.01 Å.u.–0.025 Å.u.). The echelon at the disposal of the writer, however, has not a resolving power sufficiently high to detect a difference of that order.

Sodium.

In the case of sodium at temperatures above 300° C. a brilliant yellow discharge filling almost the whole bulb was obtained. In addition to the D lines, the first four doublets of the diffuse series were identified, as well as the first three of the sharp series. The Balmer lines of hydrogen, the most likely impurity, were not visible. Hagenbach and Frey[2] observed only the D lines in the immediate neighborhood of a piece of the metal placed in the bulb, although they obtained a ring discharge showing mercury, nitrogen and carbon dioxide. Apparently their bulb was not exhausted thoroughly, nor was the sodium sufficiently vaporized.

With sodium an induction coil was used for charging the Leyden jars. With excitation similar to that used in the case of potassium and iodine, and at a temperature considerably above 300° C., it is highly probable that more and stronger lines would be brought out. As a matter of fact, evidence has been obtained of a more brilliant discharge in the case of a bulb excited in this way, but unfortunately because of a "short" which developed between the primary coil and the oven no observations were possible.

Lithium.

By courtesy of the Metallurgical Department of Queen's University, a small quantity of lithium of unknown purity was obtained, and a bulb prepared. By using an iron capsule in the side tube a small quantity of

[1] Merton, Proc. Roy. Soc., A, 679, p. 388, 1920.

[2] Hagenbach and Frey, loc. cit.

metal was vaporized and deposited in the bulb, but although the oven was heated as high as 500° C., nothing but a feeble discharge due to impurities was obtained.

MERCURY.

In common with Kowalski,[1] the writer observed with mercury, two distinct types of discharge—the first a dazzling white ring, the second a diffuse greenish glow which filled the whole bulb. The ring discharge showed numerous lines, the number increasing with increasing spark gap. One set of visual observations showed some 24 lines ranging from λ 6234 to λ 4339, twenty of which were identified with standard mercury lines belonging to the triplet, single line and combination series. Unidentified lines were observed at approximately λλ 6122, 5026, 4959. The spectrum of the greenish glow showed a continuous band upon which λ 5461 was superimposed, as well as λ 4959 and λ 4355, if the intensity was great enough. The continuous band seemed to end abruptly towards the red end at the two yellow lines.

The brilliant white discharge could be obtained at temperatures ranging from 70° to 110° C. or higher, the exact temperature at which it disappeared increasing with increasing spark gap. On the other hand, observations made with spark gap 1 mm., 2 mm., 4 mm. and 6 mm. in length indicated that the temperature at which the glow begins (110°–115°) is *independent* of the electrical intensity. The origin of the continuous spectrum, therefore, is probably closely connected with the density of the vapor. Very recently R. W. Wood [2] has made the statement that mercury vapor can be made to fluoresce only when freshly liberated from the fluid metal, and suggests that the formation of diatomic molecules is necessary for the phenomenon of fluorescence. That such a grouping of atoms is possible is evident from the work of Sir J. J. Thomson on Positive Rays, in the course of which he showed that even at the low pressures obtaining in his discharge tubes, it was possible to have clusters of four mercury atoms with a single positive charge. As such groupings would occur much more readily at vapor densities corresponding to temperatures over 100° C., it would seem that the "radiators" of the continuous spectrum are to be found in such clusters, an idea which has been previously suggested by more than one writer.[3]

With the temperature of the vapor approximately constant (at say 90° C.), observations were made at various spark lengths. It was found that below a minimum gap length (of the order of 0.5 mm.), the bright

[1] J. Kowalski, Physik. Zeit., 15, 225, 1914.

[2] R. W. Wood, Proc. Roy. Soc., A, 700, p. 362, 1921.

[3] C. D. Child, Science, Sept. 10, 1921. Horton, Phil. Mag., Vol. 22, p. 214, 1911.

white discharge gave place to a faint white luminosity whose intensity was greater in the plane of the coil, while above this length, the ring discharge appeared. At the critical stage, when the ring flashed in intermittently, the spectrum showed the five lines λλ 5791, 5770, 5461, 4916 and 4358. On increasing the gap, other lines quickly made their appearance.

In conclusion, the writer would like to emphasize the difference in the behavior of a diatomic vapor like iodine compared with that of monatomic vapors. It would seem that useful information concerning the spectra of diatomic gases, such as hydrogen, might be gained by a study of their electrodeless discharge, and it is planned to make such a study in the near future. The work planned includes an examination of the discharge in CO_2 and N_2O, to see if there is any similarity in the spectra of these two gases, whose molecules on the cubical atom theory of Lewis and Langmuir have almost identical electron structures.

Queen's University,
Kingston, Ont.,
October, 1921.

PIEZO-ELECTRIC ACTIVITY OF ROCHELLE SALT UNDER VARIOUS CONDITIONS.

By J. Valasek.

Synopsis.

Electrical Properties of Rochelle Salt Crystal are analogous to the magnetic properties of iron, the dielectric displacement D and polarization P varying with the electric field E in the same general manner as B and I vary with H for iron, and showing an *electric hysteresis* with loops distorted by an amount corresponding to the *permanent polarization* P_0, whose value is about 30 e.s.u./cm.^{3} but varies for different crystals. The *dielectric constant* ($\kappa = dD/dE$) was measured *from* $-70°$ *to* $30°$ *C.* and found to be surprisingly large, increasing from about 50 at $-70°$ to a maximum of about 1,000 near 0°. The modulus of *piezo-electric activity for shearing stresses* (δ) *varies with temperature,* $-70°$ *to* $40°$ *C.*, in a very similar manner, increasing from less than 10^{-6} at $-70°$ to a maximum of about 10^{-4} at 0°. The ratio δ/κ *varied with the electrode material,* being greater for tin foil than for mercury electrodes. The difference may be due to the alcohol used in shellacking the tin-foil electrodes on. There are other indications that δ and κ are related. The *variation of* δ *with humidity* is such as can be accounted for by the decrease in the dielectric constant of the outer layer as a result of dehydration. The change of polarization produced by pressure as measured by the change in the hysteresis loop agrees with the value found directly from the piezo-electric response, as required by Lord Kelvin's theory. Also *fatigue effects on* δ produced by temporarily applied fields are traceable to fatigue in the polarization. The *electrical conductivity below* $45°$ is less than 5×10^{-9} mhos/cm.^{3} but *from* $43°$ *to* $57°$ increases rapidly to 5×10^{-4}.

Optical Properties of Rochelle Salt as Calculated from the Natural Polarization.—Assuming only one electron is displaced the *natural period* corresponds to a wavelength of 4.2 μ and the *specific rotation* for sodium light comes out 10°, the observed value being 22°.1.

RECENTLY[1] the writer described some experiments on the dielectric and piezo-electric properties of Rochelle salt, which were made for the purpose of correlating and explaining the effects observed chiefly by Cady and by Anderson. The plates used were cut with faces perpendicular to the ă axis and with edges at 45° with the $\bar{b}$ and c axes. The present paper is a continuation of the work, the variations in the electrical properties having been studied more extensively. The apparatus and method of observation have been already described in the paper referred to above. The more important results obtained at that time can be summarized as follows:

In the case of Rochelle salt the dielectric displacement D, electric intensity E, and polarization P behave in a manner analogous to B, H, and I in the case of magnetism. Rochelle salt shows an electric

[1] J. Valasek, Phys. Rev. (2), XVII, p. 475.

hysteresis in P analogous to the magnetic hysteresis in the case of iron, the loops however being distorted by an amount corresponding to the permanent polarization of the crystal in the natural state. This point of view is very effective in accounting for many of the peculiarities observed.

In an electric field the piezo-electric activity has a maximum for a definite value of the field and decreases to a small value in both directions. The position of the maximum corresponds to the greatest rate of change of polarization with electric field in the case of the condenser experiments. In fact if force and electric field are equivalent in changing the piezo-electric polarization then the response for a given force in various applied fields must necessarily give curves of the same general nature as curves of $\partial P/\partial E$ or $\partial D/\partial E$ against E. It is permissible to interchange D and P in most cases because of the large dielectric constant of Rochelle salt.

Relation between Polarization and Piezo-electric Activity.

The activity of a piezo-electric crystal is intimately related to the natural polarization. According to Lord Kelvin this natural moment is masked by surface charges so that the crystal appears to be uncharged. This polarization or piezo-electric moment can be measured independently of the charges on the electrodes, through the distortion of the hysteresis loop. The center A of the loop is found by a consideration of symmetry and may be assumed to represent the condition of no polarization. If the natural condition of polarization is assumed to be half way between the two branches of the loop at zero field then the value of the permanent polarization P_0 is proportional to AB, Fig. 1. There being

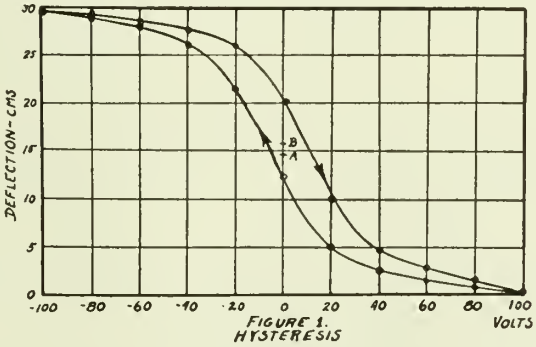


Fig. 1.

no field applied, the equation for the work done per unit charge carried through the condenser is:

$$4\pi\left(\frac{Q_0}{S} - P_0\right)t = 0,$$

so that

$$P_0 = \frac{Q_0}{S},$$

where Q_0 is the apparent average permanent charge at zero field given by AB (Fig. 1) and where S is the area of the plate. Calculation gives the value: 30 e.s.v./cm^2.

According to Lord Kelvin's theory an applied stress will change this polarization so as to create free charges on the electrodes. A force of 250 grams applied to the crystal should consequently shift the loop by an amount equivalent to the piezo-electric response for 250 grams. When this experiment was performed another, but more unsymmetrical loop, was obtained. The change in polarization by the loop method was 114 e.s.u./cm.^{2} while the piezo-electric response amounted to 121 e.s.u./cm.^{2}

The value of P_0 obtained from the hysteresis loops is only approximate because of the assumptions involved in its determination. It cannot, moreover, be fixed definitely enough to be put down as a physical constant of Rochelle salt because it varies with different specimens, besides changing with temperature, pressure and fatigue. The value $P_0 = 30$ e.s.u./cm.^{2} is thought to be a representative value and is checked by other measurements. The writer would not be surprised, however, to find other specimens giving several times this value. The change in polarization due to pressure however is derived by a differential method eliminating much of the uncertainty in measurements on one loop. The result in this case should be fairly definite, as indeed it seems to be.

Piezo-electric activity depends on both the crystalline structure and on the polarization. It is greatest for a polarization somewhat larger than normal and decreases in both directions for changes in this quantity, the polarization being changed by applying an electric field. It has been shown by the writer that this relation between activity and applied field is approximately like that of the derivative $\partial D/\partial E$ of the curve relating the dielectric displacement D and the electric field E of the crystal used as a condenser. Since this latter relation is in the form of a hysteresis loop it follows that the activity is also a double-valued function of the applied field depending on the direction of variation of the field. A curve illustrating this effect is reproduced in Fig. 2. The readings were taken in as short a time as possible to eliminate fatigue. These curves show that the piezo-electric response at zero field depends on the previous electrical treatment of the crystal. The latter fact has also been noted by W. G. Cady in the report previously referred to.

This after-effect does not persist very long but dies off exponentially with the time. The piezo-electric response or ballistic throw of the galvanometer for 250 grams has been observed to return to half value in 1 minute and to normal in over 20 minutes after fields of 150 volts have been applied for 3 minutes previously. There is a much greater after-effect in the direction of increased activity.

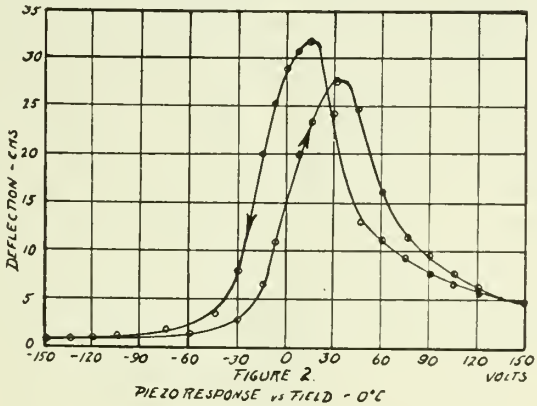


Fig. 2.

A corresponding dielectric effect is indicated by the double value of the condenser charge at zero field in the hysteresis loops. This is clearly due to a fatigue in the polarization and it also dies off exponentially with time. Herein is probably found the explanation of the "storage battery effect" described by W. G. Cady who observed that after applying a field of 100 volts for some time there was, on removal of the field, a small current which decreased gradually and flowed from the crystal as from a miniature storage battery.

The piezo-electric fatigue may well be a direct result of the fatigue in the polarization, as there seems to be a close relation between piezo-electric activity and polarization. It appears that the activity is approximately proportional to the rate of change of polarization with applied field and hence proportional to the dielectric constant. An examination of the temperature variation of the two quantities leads to this conclusion. It is further confirmed as regards field variation by the fact that the relation of activity to applied field is like $\partial D/\partial E$ vs. E where $\partial D/\partial E$ is merely the instantaneous value of the dielectric constant κ. As an approximation we can write the piezo-electric modulus δ proportional to κ:

$$\delta = A \cdot \kappa.$$

If this equation were exact A would be a fundamental piezo-electric constant of the substance, being of the order of 1×10^{-7} between $-20°$ C. and $+20°$ C. At some temperatures and for some exceptional specimens the relation does not seem to be so simple.

Effect of Moisture on Piezo-electric Properties.

In order to investigate the effect of dryness on the activity of Rochelle salt, some phosphorus pentoxide was enclosed in the chamber containing the crystal. The crystal soon started to dehydrate and after a few days was covered by a white coating. The piezo-electric throw for a load of 250 grams continually diminished. When the response was tested at different fields a more interesting fact was observed. Besides the decrease in response, the maxima were displaced along the field axis into a condition of greater polarization. This is shown by Fig. 3, the curves

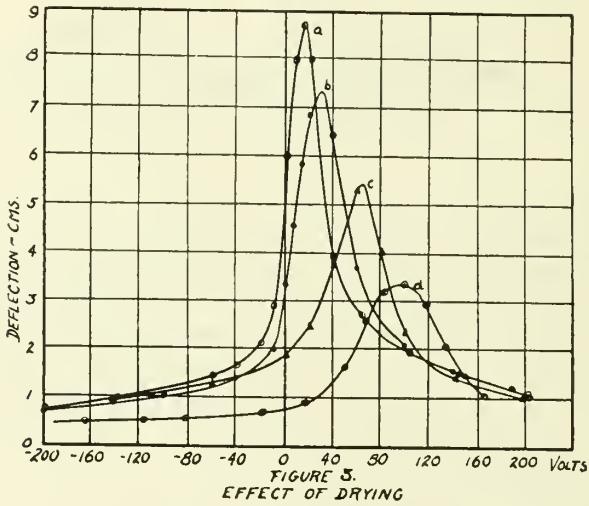


Fig. 3.

being taken after the lapse of the following times: (*b*) 1 day, (*c*) 3 days, (*d*) 12 days.

The decrease in the maxima and also their displacement is in the same direction as, and may be entirely due to, the effect of different dielectric properties of the crystal and of the dehydrated layer. In other words the presence of a layer of inactive dielectric of relatively low specific inductive capacity will diminish the charge on the plates due to the polarization of the central active layer, and thus decrease the piezo-electric response. It will also diminish the effective field across the active layer making it necessary to increase the potential difference

between the plates to produce the same field across the inner layer, thus shifting the position of maximum activity. The effects due to uniform layers can be readily calculated. Let P_0 be the polarization produced in the middle layer by pressure, let P_1 and P_2 be the electrically induced polarizations in the dielectrics 1 and 2 respectively (Fig. 4). Since the dielectric displacement is solenoidal we have:

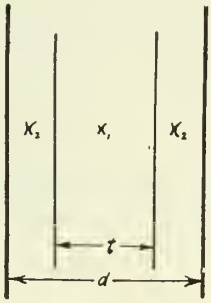


Fig. 4.

$$D' = E_1 + 4\pi P_1 + 4\pi P_0 = E_2 + 4\pi P_2 = 4\pi\sigma.$$

Since

$$P_1 = (\kappa_1 - 1)E_1 \qquad \text{and} \qquad P_2 = (\kappa_2 - 1)E_2$$

we can write

$$D' = \kappa_1 E_1 + 4\pi P_0 = \kappa_2 E_2.$$

The difference of potential between the plates is zero so that, replacing P_0 by σ_0:

$$\begin{aligned} 0 &= E_2(d - t) + E_1 t \\ &= \frac{4\pi\sigma}{\kappa_2}(d - t) + \frac{4\pi}{\kappa_1}(\sigma - \sigma_0)t, \end{aligned}$$

giving:

$$\frac{\sigma}{\sigma_0} = \frac{Q'}{Q} = \frac{\kappa_2 t}{t(\kappa_2 - \kappa_1) + \kappa_1 d}.$$

This gives us a relation between the piezo-electric response at zero field of the crystal with the dry shell and of the same crystal before it dried. The assumption is made that the elasticity of the shell is equal to that of the crystal so that a given total force produces the same polarization in the crystalline portion.

The position of the maximum will be changed to another value of total potential difference on the crystal. Let V be the total potential drop and V' be the drop across the crystalline part. When there is no dehydrated layer present

$$V = V' = dE,$$

where E is the field strength in the dielectric. When there is a layer of uniform thickness $(d - t)/2$ on both faces then

$$V = (d - t)E'' + tE',$$

where E'' and E' are the field strengths in the dielectrics 2 and 1 respectively. The dielectric displacement

$$D = \kappa_2 E'' = \kappa_1 E' + 4\pi P_0,$$

is solenoidal, and we can eliminate E'' from equations above and write:

$$V' = dE = (d - t)\frac{\kappa_1}{\kappa_2}E' + tE' + 4\pi P_0\left(\frac{d - t}{\kappa_2}\right).$$

Since the last term is small compared to the rest of the expression, this gives:

$$\frac{E'}{E} = \frac{\kappa_2 d}{t(\kappa_2 - \kappa_1) + d\kappa_1}.$$

The following quantities were measured and substituted in these equations.

$$\kappa_1 = 1000, \qquad d = 0.22 \text{ cm.},$$
$$\kappa_2 = 180, \qquad t = 0.14.$$

The quantity t is an average obtained by breaking the crystal in several places and it is probably not very accurate because of the irregularity of the outer layer. We should, however, get a rough check on the plausibility of the proposed explanation. We find that

$$\frac{Q'}{Q} = 0.24$$

and that

$$\frac{E'}{E} = 0.38.$$

While the values of Q'/Q and E'/E from the maxima of curves a and d of Fig. 3 are respectively 0.39 and 0.33. The agreement is not as good as could be desired even after making allowance for the difficulties in estimating t. Possibly there is a true humidity effect with respect to piezo-electric activity but the above shows, at least, that it is quite small.

Piezo-electric Activity and Temperature.

In order to investigate the variation of activity with temperature, the chamber holding the crystal was immersed in CO_2 snow. After everything was thoroughly cooled and at $-75°$ C., the chamber was allowed to heat up. Above $-35°$ C. an electric heater was used. It was wound on a glass jar and insulated from the crystal chamber by a felt jacket. This jar was immersed in an oil bath to steady the heating rate while the felt eliminated any rapid changes of heating of the crystal. The current was gradually increased so as to keep the rate of heating uniformly between $\frac{1}{2}°$ and $1°$ C. per minute so as to eliminate thermoelastic stresses. The temperature was measured by means of a copper-constantan thermocouple directly soldered to an electrode on the crystal. In this way the actual temperature of the crystal itself was measured.

When the piezo-electric response or galvanometer throw foi 250 grams was measured at the various temperatures for the first specimen the curve of Fig. 5 was obtained. This was duplicated to check the second

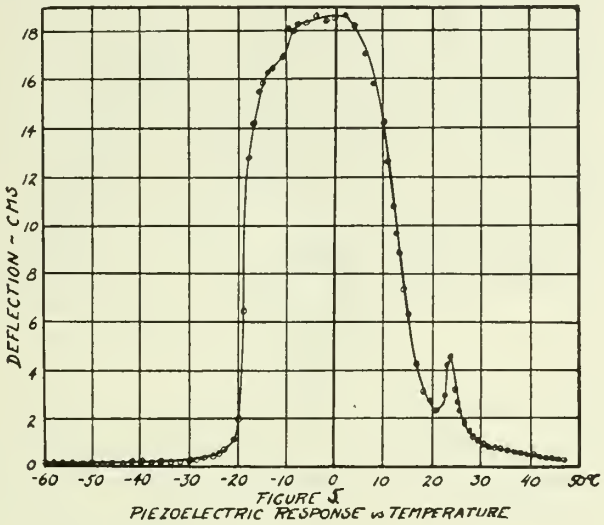


Fig. 5.

maximum. At − 70° C. the piezo-electric activity is comparatively negligible. As the temperature is raised slowly the activity stays small until − 30° C. is reached. At − 20° C. it is rising very rapidly, reaching a maximum at about 0° C. It decreases again but at 23° C. comes to a small but sharp maximum from which it diminishes slowly, becoming very small at + 50° C. The magnitude of the second maximum varies with the temperature at which heating begins. This second maximum was found in the case of two crystal plates provided with tinfoil electrodes attached by shellac.

Three other crystals were prepared with electrodes of mercury held against the crystal by two rectangular cups attached by wax. The thermocouple wires were immersed in the mercury. None of the crystals so prepared gave the second maximum. Moreover, none of them were as active as those used above. The variation of piezo-electric response of these specimens is shown in Fig. 6. The increase at − 30° to − 15° C. and the decrease at + 20° C. to + 30° C. are remarkably consistent. Between − 15° and + 20° C., however, they each show different characteristics. These mercury electrode crystals seemed to give more constant results than the crystals with tinfoil electrodes attached by shellac.

It was then suspected that the increased response of the crystal with

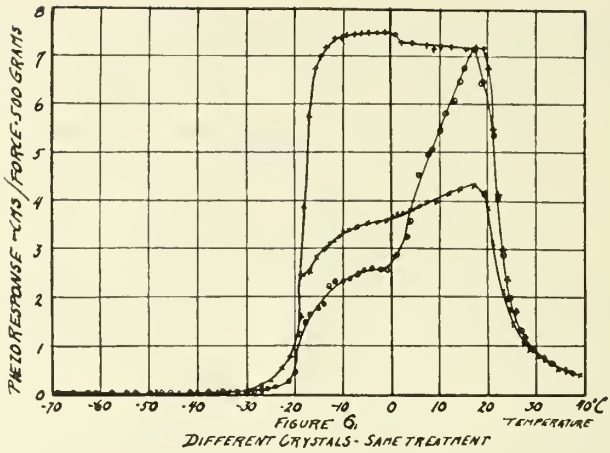


Fig. 6.

tinfoil electrodes and the presence of the second maximum was in some way due to the penetration into the crystal of the alcohol solvent of shellac. Accordingly one of the crystals originally with mercury electrodes was provided with the other type. As soon as the shellac was sufficiently dry, Curve *b*, Fig. 7 was obtained, the response originally

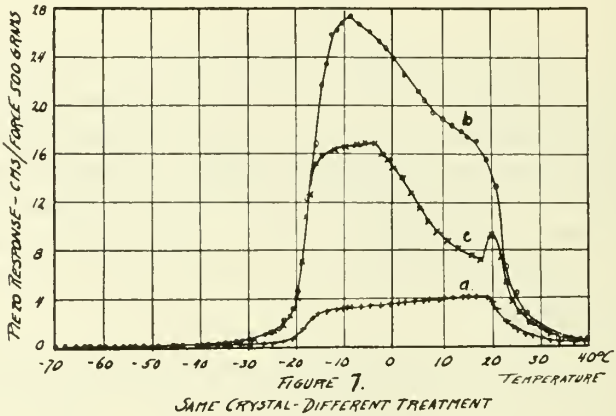


Fig. 7.

having followed Curve *a*. The sensitivity increased seven-fold at some temperatures but there was no second maximum. In two weeks the characteristics had changed to those shown in Curve *c*, seemingly checking the suspicion that alcohol was responsible for the second maximum and for the increased sensitivity. It would be interesting to use alcohol cup electrodes and investigate the continuous effect of alcohol soaking into the crystal. The effect is probably not chemical.

In a paper on the piezo-electric effect on Rochelle salt, A. M. Nicolson[1] describes a method for desiccating the crystals by soaking in alcohol and heating, thus making them stronger and more sensitive. The writer is certain, from his work on the subject, that complete desiccation will make the crystal entirely inactive. In the above method, apparently, the treatment is not prolonged enough to completely dehydrate more than a shell around the crystal and its effectiveness may be connected with the penetration of the alcohol into the crystal. The heating at 40° C. may also be effective in allowing a rearrangement and recrystallization of some of the molecules or groups not properly oriented. W. G. Cady, as well as the writer, has observed that heating the crystal will usually increase its sensitivity permanently, although sometimes the reverse is true.

An interesting side-light on the temperature variation of piezo-electric activity is offered by a study of curves like that of Fig. 2 but at different temperatures. They show that the effect of temperature is not so much to change the piezo-electric activity as to shift the position of the maximum from one value of the field to another. This is probably connected with the variation of the dielectric constant with temperature which will be taken up presently.

The charging throws of the crystal used as a condenser show variations similar to those of the activity except that they do not tend to zero but to a constant value at the lower temperatures. The crystals giving the second maximum on the piezo-electric curve show a similar peculiarity here. The crystals with the mercury electrodes give more regular curves. At 20° to 25° C. the crystals of both types begin to conduct, causing a steady drift of the galvanometer. Experiments seem to indicate that Ohm's law holds at least approximately. The conduction was at first thought to be electrolytic because of the manner in which Rochelle salt melts. Instead of real melting it appears that the crystal dissolves in its water of crystallization which is set free at 55° C. The desiccated crystal, however, decomposes into a tarry product and emits heavy white fumes above 150° C., without melting. The dehydrated crystal also begins to conduct above 20° C., making it probable that electronic and not electrolytic conduction is observed.

Measurements of conductivity were made on the natural crystal at various temperatures up to its liquefying point. The values obtained after the conductivity was sufficiently large to use a Wheatstone bridge are as follows:

[1] A. M. Nicolson, Proc. Am. Inst. Ele. Eng., Vol. 38, p. 1315 (1919).

TABLE I.

Temperature.	Conductivity.
Less than 43° C.	Less than 0.5×10^{-8} mhos/cm³.
43	0.5×10^{-8}
45	1.0×10^{-8}
47	0.3×10^{-7}
49	0.5×10^{-7}
51	0.5×10^{-6}
53	0.6×10^{-4}
54	1.7×10^{-4}
57	5.0×10^{-4}
Greater than 57	5.0×10^{-4}

At temperatures below 20° the dry crystal is a fairly good insulator having a specific conductivity of 5×10^{-12} mhos/cm.³ at 0° C. The conductivity decreases slightly at still lower temperatures. In all these measurements the surfaces were thoroughly dried by the presence of phosphorus pentoxide in the crystal chamber.

TABLE II.

Temp. Cent.	Dielectric Constant.		Piezoelectric Modulus.	
	A	*B*	*A*	*B*
−70	71	42	0.041×10^{-5}	0.017×10^{-5}
−50	85	50	0.068 "	0.017 "
−30	140	146	0.41 "	0.065 "
−20	386	252	5.4 "	1.08 "
−10	943	924	18.9 "	6.07 "
0	1,380	956	22.9 "	6.75 "
10	1,100	928	18.9 "	7.42 "
20	688	645	13.5 "	8.10 "
30	423	146	2.2 "	1.08 "
	Conduction commences		0.41 "	0.41 "

Table II. gives values of the dielectric constants for a field changing from 0 to 880 volts/cm. and of the piezo-electric modulus δ_{14} for shearing stresses of 220 grams/cm.². The modulus δ_{14} is defined by the relation given by Voigt $\sigma_1 = -\delta_{14} Y_z$ where σ_1 is the surface density of charge and Y_z is the shearing stress producing it. The given values are thought to be the most representative in each case. They are subdivided into two classes, according to whether the electrodes were tinfoil attached by shellac (column *A*) or mercury in direct contact with the crystal (column *B*). The former method is the most convenient to use in general practice, but the latter is thought to give more exactly the properties of Rochelle salt in the direction of the ă axis. The dielectric

constants are surprisingly large, a fact noticed by Pockels[1] who supposes that this is due to "internal conductivity." The writer however has measured separately the conductivity at these temperatures and is of the opinion that this is a true dielectric constant arising from polarization of the dielectric, and for this reason being so closely related to the piezo-electric effect. Because of the relatively low specific inductive capacity of the desiccated crystal it is thought that the high specific inductive capacity of Rochelle salt is partly due to the water molecule.

Magnetic Analogy.

There seems to be a strong analogy between the behavior of Rochelle salt as a dielectric possessing hysteresis and having an exceptionally large dielectric constant, and the phenomena of ferromagnetism. Accordingly some of the features of Weiss's theory of magnetism may find their counterpart in the phenomena in Rochelle salt. Weiss[2] plots the susceptibility against the reciprocal of the absolute temperature and finds that the curve may be represented by a succession of straight lines. He interprets the sudden changes in slope as due to changes in the number of magnetons. If the data of Figs. 8*a* and 12 are plotted against the reciprocal of the absolute temperature one likewise gets what may be considered to be a succession of straight lines. Actually however there occur rounded corners where the curves suddenly change direction. This may be due to slight non-uniformity in heating which occurred in spite of the precautions taken. It is considered that the straight portions are at least as definite as those shown in Weiss's paper. The most abrupt changes are at $-20°$ C. and at $+20°$ C. These may accordingly be considered as the "Curie points" in Rochelle salt.

Relation to Optical Properties.

Some of the optical properties of Rochelle salt can be at least approximately found from the electrical data given. In the course of this calculation it is of course necessary to introduce some assumptions notably as to the nature of the permanent polarization. If one knew just how the permanent polarization was produced he could find the free period of this mechanism. The data needed are the force per unit displacement f and the mass m of that part of the molecule. The wave-length corresponding to the free period is given by the expression

$$\lambda = 2\pi c \sqrt{\frac{m}{f}}$$

c being the velocity of light.

[1] Pockels, Lehrbuch der Krystaloptik, p. 508.

[2] P. Weiss, J. de Physique, Vol. 1, p. 968 (1911).

Let us assume for simplicity that only one electron is involved in the creation of the permanent moment. The quantity f can be derived from the value of the permanent moment $P_0 = 30$ e.s.u./cm.^{2} and from the displacement of the electron producing it. Since the force on an electron inside a dielectric of polarization P_0 is roughly equal to $\frac{1}{3}P_0e$[1] the expression for the wave-length may be put in the form:

$$\lambda = 2\pi c\sqrt{\frac{3md}{P_0e}}\ .$$

The value of d, the displacement of the electron, can be found as follows:

Taking 30 e.s.u./cm.^{2} as the natural polarization, the moment per molecule is obtained by dividing by the number of molecules per c.c., the result being 7.1×10^{-21} e.s.u. In each of these molecules there are 140 electrons, this being the sum of the atomic numbers of the constituent elements in Rochelle salt. If we suppose as above that only one of these is effective in producing the piezo-electric moment, its displacement from the center of force of the rest of the molecule will be $d = 2.7 \times 10^{-11}$ cm. It would of course be more reasonable to suppose that at least several of the electrons are displaced by different amounts, and to the extent that we do this the value calculated above becomes smaller.

Using these values of P_0 and d for the simple case treated above we find for the wave-length the value:

$$\lambda = 4.2\ \mu.$$

Coblentz[2] shows the presence of fairly strong absorption in this region of the infra-red. This may, however, be due to the water of crystallization and not to the cause cited above. These two possibilities should be distinguishable experimentally because the character of the absorption due to these electrons should change greatly with the temperature, as the piezo-electric elasticity or force per unit displacement of the electrons changes.

The natural period as found above should be the same as that involved in rotatory dispersion formulæ, since both the piezo-electric effect and optical rotation are due to an unsymmetrical or twisted structure of the molecule. J. J. Thomson[3] gives an approximate formula for the specific rotation, namely:

$$\rho = \frac{e^2dp^2}{c^2Mmn^2}\ ,$$

[1] H. A. Lorentz, Theory of Electrons, p. 306.

[2] W. W. Coblentz, Infra Red Spectra, Vol. 2, p. 38.

[3] J. J. Thomson, Phil. Mag., Dec., 1920.

in which e is the charge of the electron, c is the velocity of light and M and m are the masses of the molecule and of the electron, d is the radius of the molecule, p is the free period, and n is the frequency for which ρ is to be calculated. Using the value of p derived from piezo-electric data we find for sodium light the specific rotation of the order of magnitude of 10°, the tables giving 22.1°. Considering the fact that so little is known of the structure of the Rochelle salt molecule, the approximation is fair.

The writer is indebted to Professor W. F. G. Swann, who initiated this research and gave many helpful suggestions, and to Dr. W. R. Whitney, Director of the Research Laboratory of the General Electric Company, whose presentation of two beautiful crystals made the work possible.

Physical Laboratory,
University of Minnesota.

MINIMUM SOUND ENERGY FOR AUDITION FOR TONES OF HIGH FREQUENCY.

By C. E. Lane.

Synopsis.

Minimum Energy for Audition for Tones above 2000 p.p.s.—Using the new tone generator developed by Hewlett as the source of sound, experiments were carried on at night and out of doors on a platform raised 5 meters above the ground and with the listening ear 150 cm. from the source. The amplitude of vibration of the diaphragm of the generator was calculated from the electrical input, and from it the corresponding sound intensity at the ear of the listener was computed, assuming the amplitude of the sound wave at the diaphragm the same as that of the diaphragm and correcting for the concentration of sound around the axis of symmetry as experimentally determined. No correction for the effect of the listener's head, however, was made. *Sensitivity frequency curves* for eight normal ears, ages 19 to 35 years, are reproduced. The minimum audible intensity was found to remain practically constant at 7×10^{-8} ergs per cm.^{2} for frequencies from 2,000 to 14,000 p.p.s., but above 14,000 the sensitivity decreased more and more rapidly until at between 18,000 and 20,000 p.p.s., depending on the individual, an intensity of 0.1 erg per cm.^{2} was inaudible. *A variation with age* was observed, the upper frequency limit being considerably higher for children and lower for older persons than for normal young adults.

Distribution of Sound Intensity around a Hewlett Tone Generator for 2,000 to 15,000 p.p.s. was determined roughly by studying the minimum amplitude for audition as a function of the angular position of the listener with reference to the axis of symmetry. The sound is largely concentrated in a cone of about 20°, the angle decreasing as the frequency increased, so that for 10,000 p.p.s., for instance, the intensity 150 cm. along the axis was fifty times as great as if the distribution had been spherical.

Introduction.

THE purpose of this investigation was to determine in absolute units the sensitivity of the ear for tones ranging from 2,000 p.p.s. to the upper limiting audible frequencies. Experiments have been made by many different observers for determining the minimum amount of sound energy for audition but most of these investigations have been concerned with tones of frequencies below 4,000 p.p.s. Little work at the higher frequencies has been done because of the limitations of the apparatus used. In the early work done by Wien[1] and in the recent work of Kranz[2] the ear was shown to reach a maximum sensitivity in the neighborhood of 2,000 p.p.s. At the Chicago meeting of the National Academy of Sciences, November 14, 1921, Fletcher and Wegel presented some results

[1] Archiv. für die gesamte Physiologie, Vol. 97, pp. 1–57, 1903.

[2] Phys. Rev., (2) xvii, 1921, page 384.

which they had obtained for sensitivity of normal ears. These results showed that the ear reached a maximum sensitivity in the neighborhood of 2,000 p.p.s. and then remained constant to 4,000 p.p.s. No attempt was made by them to obtain measurement in absolute units at higher frequencies.

Apparatus and Method.

In this investigation the new tone generator,[1] developed by C. W. Hewlett, was used as a source of sound. The radiating surface of the tone generator consisted of a thin aluminum diaphragm, 10 cm., in diameter, actuated by a flat coil carrying variable polarizing (direct) and alternating currents. One side of the diaphragm was wholly unobstructed for the free passage of sound waves from its surface, while the type of coil used did not greatly affect the passage of sound from the opposite side. Amplitudes of motion of the diaphragm for minimum audible sounds were calculated from the corresponding current input by using Hewlett's theory, adapted to suit the particular arrangement used. At any frequency it can be shown that the amplitude of motion of the diaphragm is proportional to the product of the direct and alternating currents and that the energy radiated is proportional to the square of this product.

The work was done out of doors with the observer on a small platform five meters above the ground and the sound source 1.5 meters from his ear. This arrangement was assumed to reduce reflections from the ground to an amount negligible compared to the energy received directly. It is evident that the ratio of direct energy from the apparatus to reflected energy from the ground, assuming the most unfavorable conditions, would be of the order of magnitude of the ratio of $(2 \times 5)^2 : 1.5^2 = 44 : 1$.

The work was done at night to minimize the interfering effect of noise. The face of the sound source was turned toward the observer and the ear to be tested was turned toward the source. It was found by trial that it was not necessary to close the other ear on account of the sound shadow of the head.

The amplitude of the sound wave was assumed to be the same at the diaphragm surface as that of the diaphragm. The total energy emitted was calculated assuming it to be the same as would be radiated in a plane wave. Therefore, the total amount of sound energy, E_t, given off by one side of the diaphragm per second would be given by—

$$E_t = \tfrac{1}{2} S \rho V A^2 \omega^2.$$

S = area of each side of the diaphragm.

[1] Phys. Rev., (2), xix, p. 52, 1922.

ρ = density of the air.
V = velocity of sound in air.
A = amplitude of vibration of the diaphragm.
ω = 2π times the frequency.

In a simple spherical distribution the energy flux per sq. cm. at a distance of D from the source would be $E_t/2\pi D^2$. This is an average value for energy flux on the surface of a hemisphere of radius D. If R is the ratio of the actual value, J, at the position of the observer's ear to the average value, then

$$J = \frac{E_t R}{2\pi D^2}$$

R was determined for each frequency from the following considerations.

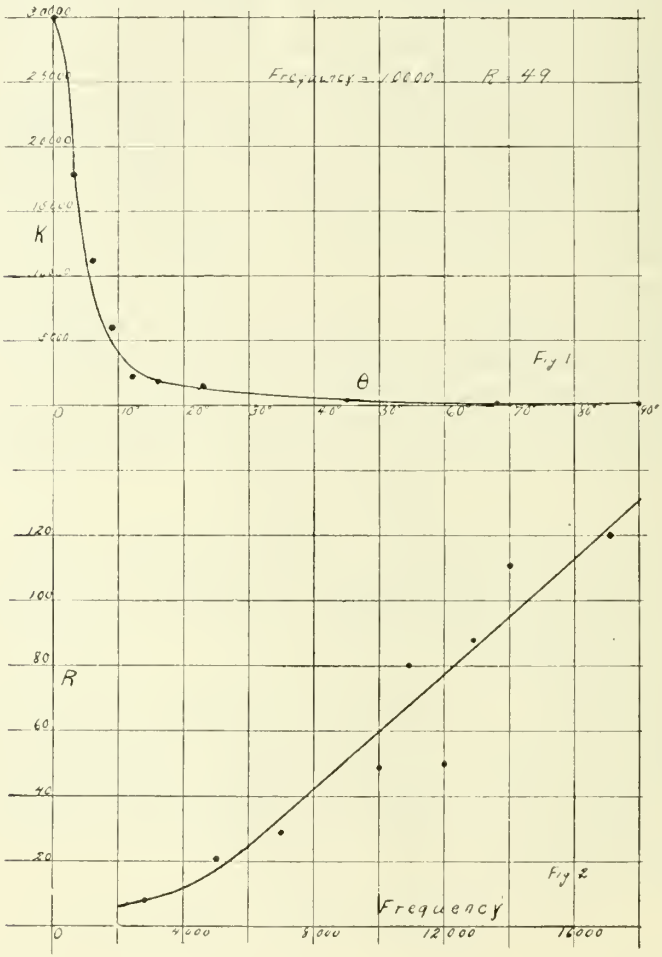


Fig. 1.
Fig 2.

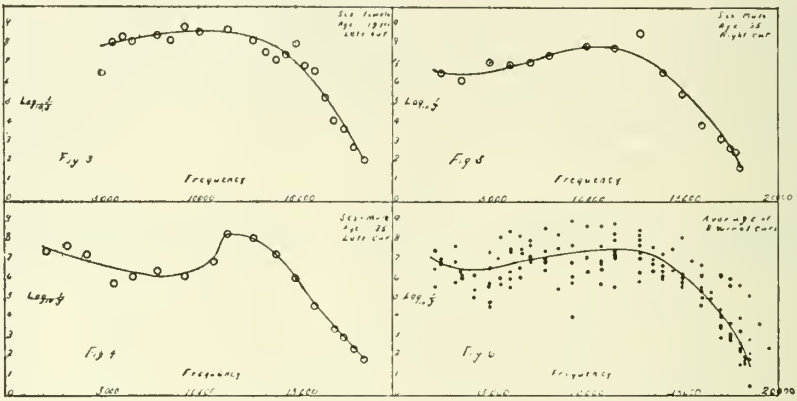
The sound field was assumed to be symmetrical with respect to the axis of the diaphragm. This axis (horizontal) also passed through the ear of the observer. The relative distribution of energy flux on the surface of a sphere of radius D was determined by calculation from the measurement of minimum audible amplitude of the diaphragm as it was turned about a vertical axis, through its center, through an angle of 180°. Fig. 1 shows energy density so determined at 10,000 p.p.s. plotted in arbitrary units as a function of the angle. Between 90° and 180° it is roughly symmetrical with that between 90° and 0°. It is seen that the major part of the energy from the side of the receiver toward the observer is concentrated within a cone making an angle of 20° at the center of the diaphragm. The assumption that all of the energy radiated from one side of the diaphragm is contained in the corresponding beam indicated in Fig. 1 is justified on the basis of the theory of radiation of a plane wave from a circular aperture. Using this distribution curve and the calculation of the total energy flux, as determined from the tone generator theory, the energy flux per sq. cm. could be calculated at any point on the sphere of radius D. The ratio, R, of the energy flux density at the position of the ear to that which would be obtained in a simple spherical distribution was found to be 49 : 1 at the frequency illustrated in Fig. 1. Fig. 2 is a plot of R as a function of frequency. This shows, as might have been expected, that the energy becomes more and more concentrated in a narrow beam as the frequency increases.

Results and Conclusions.

The value of J was determined at different frequencies for eight normal ears. In order to show the variation in sensitivity of the ears graphically the $\log_{10} (1/J)$ was plotted against frequency. Logarithms were necessary because of the wide variation of sensitivity of the so-called normal ears. The audiograms—sensitivity frequency curves for the ears—thus obtained are shown in Figs. 3, 4, 5 and 6. Figs. 3, 4 and 5 are audiograms for individual ears, Figs. 4 and 5 being the left and right ears of the same individual. Fig. 6 shows the results obtained for eight ears from seven different individuals. Each of the persons from whom the data were obtained was between 19 and 35 years of age. The value of J for a frequency of 2,000 p.p.s. as obtained by taking the mean value of $\log_{10} (1/J)$ for this frequency, was found to be 7×10^{-8} ergs. This is about three times the value given by Kranz, about seven times the value obtained by Fletcher and Wegel[1] and 30,000 times the value given by Wien for the same frequency. But little variation in the ear sensitivity

[1] R. M. S. pressure in dynes per sq. cm. is equal to $6.5 \sqrt{J}$.

from this was noted until a frequency of 14,000 p.p.s. was reached. As the frequency was increased above 14,000 p.p.s., the sensitivity decreased more and more rapidly. Between 18,000 p.p.s. and 20,000 p.p.s., a frequency was reached for each individual ear at which it was no longer



Figs. 3, 4, 5, 6.

possible to produce a tone of sufficient intensity for audition by means of the apparatus used. The mean value for J at a frequency of 18,500 was about .1 erg. If it had been possible to produce tones of greater intensity, no doubt the threshold of audition would have been found at a higher frequency. However, it would appear from the rapid decrease in sensitivity at these high frequencies, it would be necessary to increase the intensity of the tone by a very large amount in order to raise the threshold to a frequency noticeably higher.

Special attention is called to the age of the individuals tested. There is certainly a great variation in ear sensitivity, especially for high frequencies, with the age of the individuals. Some qualitative results were obtained which show that children under fifteen years of age may hear tones as high as 25,000 cycles when the intensity is no greater than for a value of J corresponding to .1 erg. On the other hand, persons past fifty years of age are not able, as a rule, to hear such high frequencies as were heard by the individuals whose ears were tested.

There are a few sources of inaccuracy in the results obtained which should be mentioned. The value of R varies a great deal from the mean value. However, this error is small and may be neglected when we consider the fact that the observational errors for the same frequency and the same individual may themselves vary by as much as 50 per cent. It should also be mentioned here that the work was not done under

perfectly quiet conditions and the very slight disturbance would make the ear appear less sensitive than it actually is. The work was done at night but some noise was present due to the sound of insects. J has been defined as the amount of sound energy necessary for audition flowing per second through a sq. cm. It is evident that the value of J obtained by this method only gives the amount of energy which would flow through a sq. cm. were the head not at the position for which J was calculated. Further, if it may be assumed that the sound is completely absorbed by the head, the figures given for sensitivity represent the energy per sq. cm. flowing into the ear. If the head may be assumed to be a plane reflector the actual energy density at the ear is twice that in the first case. The actual condition is between the two extremes but in all probability nearer the second. However, it will be seen from the figures that a factor of two would involve a negligibly small relative error.

In conclusion I wish to express my appreciation of the assistance rendered during the experimental work by Dr. C. W. Hewlett and other members of the staff of the University of Iowa as well as the suggestions offered in the interpretation of the data by various members of the scientific staff of the Western Electric Company, Inc.

Physics Laboratory,
State University of Iowa,
June, 1921.

THE SENSITIVITY AND PRECISION OF THE ELECTROSTATIC TRANSMITTER FOR MEASURING SOUND INTENSITIES.

By E. C. Wente.

Synopsis.

Electrostatic Transmitter of Constant Sensitivity.—(1) *Characteristics.* This instrument is the same in principle as that described in 1917, but certain changes have been made which, as proved by actual tests, render the sensitivity independent of changes of temperature, pressure and humidity. The sensitivity is also found to be constant over a long period of time. By means of a piston-phone and a thermophone, for which corrected formulæ are available, both the absolute sensitivity and phase lag were determined for frequencies of from 10 to 12,000 cycles. Eight transmitters similarly constructed give the same curves within 20 per cent. With a steel diaphragm 0.0051 cm. thick having a natural frequency of 7,000 cycles, and with an air gap of 0.0025 cm., the mean sensitivity is about 0.35 millivolt/dyne. (2) *Use with an amplifier for measurement of sound intensity.* Combined with an amplifier of ordinary design the instrument has an over-all sensitivity which is practically uniform from 25 to 8,000 cycles. It is therefore remarkably well adapted for the measurement of the intensities of complex tones and tones of changing pitch and for use with an oscillograph for recording sound waves. On the other hand, if sounds of a definite pitch are to be measured, the apparatus can be made highly selective and almost any desired sensitivity can be obtained by using a tuned amplifier in connection with a vibration galvanometer.

THE writer some years ago published a paper[1] in this journal on the use of an electrostatic transmitter for the absolute measurement of sound intensities. The transmitter, as there described, consisted essentially of a thin metal diaphragm under tension separated by a small distance from a plane metal plate, the plate and the diaphragm forming the two electrodes of an air condenser. Data were given which showed that the instrument had a uniform sensitivity over a wide range of frequencies and so was especially adapted for the measurement of intensities of sounds of various frequencies.

The relation between sensitivity and frequency was determined by means of a thermophone and also, at the lower frequencies, by means of a piston-phone. But, as the two methods did not yield the same absolute values, doubts were cast upon the accuracy of the results. Since then the theory of the thermophone has been further developed and corrected formulæ for its acoustic efficiency have been obtained.[2] The pressures calculated by these new formulæ have been found to agree with those

[1] Vol. X., No. 1, p. 39, July, 1917.

[2] E. C. Wente, Phys. Rev. (2), XIX, p. 666.

given by a piston-phone, so that an absolute calibration of a transmitter may now be made with the thermophone which is dependable over a wide frequency range.

The particular electrostatic transmitter described previously had a natural frequency of nearly 17,000 cycles per second. As this frequency is considerably beyond the region which is covered in most acoustic measurements, it is desirable to construct an instrument with a lower natural frequency and thereby obtain greater sensitivity. Dr. I. B. Crandall [1] has shown theoretically how the natural frequency and damping of an electrostatic transmitter may be given almost any desired values by cutting grooves of the proper size in the back plate.

The transmitter which is here described has a natural frequency slightly over 10,000 cycles per second and a damping constant of 14,000. The sensitivity-frequency characteristic is such that an amplifier may readily be constructed so that the sensitivity of the amplifier and transmitter combined shall be nearly the same from 25 to 8,000 cycles per second. Tests have shown that the sensitivity of the transmitter is closely maintained under various atmospheric conditions for a long period of time.

Construction of the Transmitter.

A sectional drawing of the transmitter is shown in Fig. 1. The transmitter differs from the instrument previously described in several essential respects. The diaphragm, *A*, is made of 0.002 inch (0.0051 cm.) steel and is stretched so that its natural frequency in free air is 7,000 cycles per second. Annular grooves are cut into the face of the back-plate, *B*, to give the diaphragm the desired natural frequency and damping. The length of the air-gap is 0.001 inch (0.0025 cm.). To keep out moisture, the space surrounding the back-plate is sealed off completely from the outside air. A thin rubber diaphragm, *C*, is provided to keep the pressure on the two sides of the steel diaphragm substantially equal under all conditions of temperature and atmospheric pressure.

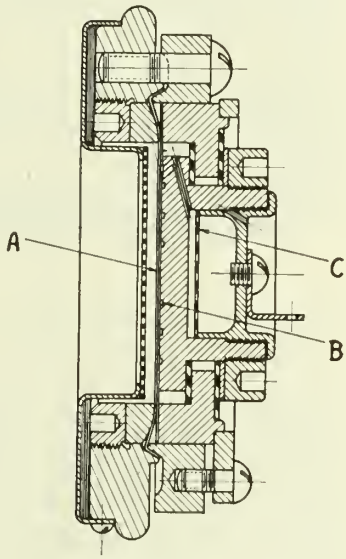


Fig. 1.

Sectional view of the electrostatic transmitter.

[1] E. C. Wente, Phys. Rev., (2) XI., 450 (1918).

CALIBRATION OF THE TRANSMITTER.

The open-circuit voltage of the transmitter per unit of pressure has been measured with the piston-phone for the frequency range of 10 to 200 cycles per second and with a thermophone for the frequency range of 60 to 12,000 cycles per second. Both of these instruments have been described in another paper.[1] The method of measurement was virtually the same as previously described,[2] except that an a.c. potentiometer[3] was used in place of a thermo-couple and galvanometer. The polarizing voltage in all cases was 200.

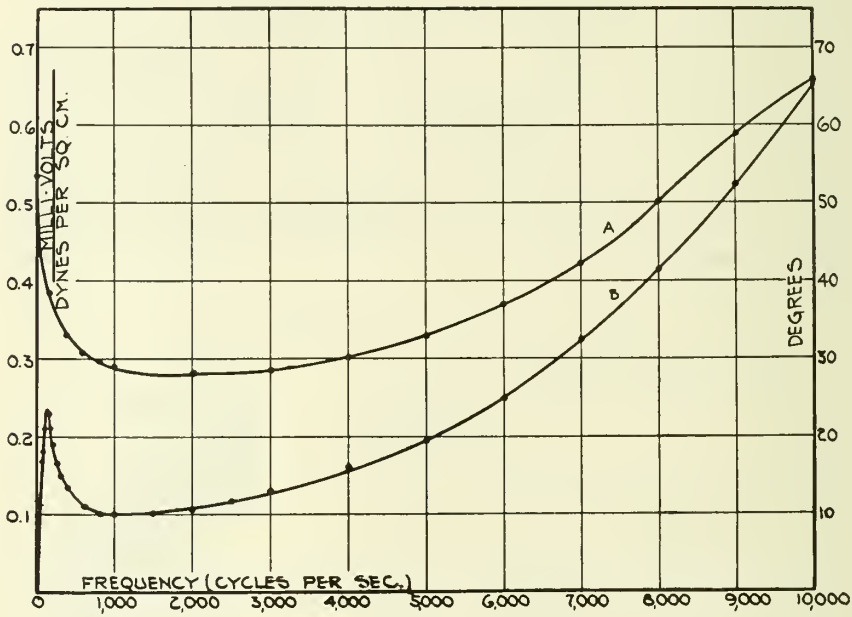


Fig. 2.

Sensitivity-frequency characteristic of the electrostatic transmitter. *A*. Volts per unit of pressure. *B*. Phase lag of e.m.f. behind pressure.

Fig. 2 gives the calibration curve obtained by averaging the results for eight transmitters. Between 25 and 8,000 cycles the calibration curve of none of the individual transmitters differs from this average curve by more than 20 per cent. To make all the transmitters exactly alike would require extreme precautions in construction, which would add considerably to their cost. However, even if there is a considerable variation in the mechanical constants of the individual instruments, we

[1] E. C. Wente, The Thermophone, loc. cit.

[2] E. C. Wente, PHYS. REV., (2) X., 51 (1917).

[3] E. C. Wente, Journal A. I. E. E., XL, p. 900, 1921.

may obtain a very nearly correct value of the calibration curve of any particular instrument by measuring the sensitivity at 200 cycles with the piston-phone and multiplying the ordinates of the curve given in Fig. 2 by the ratio of the value so obtained to the value of the ordinate of this curve at 200 cycles. For the eight calibrated transmitters the difference between the true calibration and the values obtained by this latter method was at no point greater than 12 per cent. for frequencies lying between 20 and 8,000 cycles per second, and for most of the transmitters the difference was nowhere greater than 5 per cent. This difference is small enough to be neglected in practically all acoustic measurements. Unless a precision greater than five per cent. is required it is therefore unnecessary to make any other measurements on transmitters of this type than that of the determination of the sensitivity at 200 cycles by means of the piston-phone, a measurement which may be made in a few minutes.

Fig. 2 shows that the sensitivity of the transmitter is not independent of frequency. However, since the transmitter is generally used with an amplifier, the sensitivity varies with the frequency in a desirable way. An amplifier as normally constructed has an amplification characteristic which is nearly proportional to the reciprocal of the efficiency characteristic of the transmitter. At any rate, an amplifier can readily be designed so that the sensitivity of the transmitter and amplifier combined is practically uniform from 25 to 8,000 cycles.

For the frequency range of 60 to 10,000 cycles a determination was also made of the phase relation between the pressure exerted on the diaphragm and the voltages generated by the transmitter. The values that were obtained are also plotted in Fig. 2. The maximum in the curve at 200 cycles is due to the fact that the damping of the diaphragm by the air in the gap increases with decrease in frequency.[1]

Variation of Sensitivity with Time.

To determine the change in sensitivity of the transmitter with time under ordinary conditions of use it would be necessary to make measurements extending over a long period. The more practical method of subjecting the transmitter to a higher temperature for a shorter period of time was therefore adopted. A transmitter was heated daily for five or six hours to about 45° C. and then allowed to cool to room temperature. No change in efficiency was observable even after this process had been continued for more than two weeks. The precision of the measurements was about 2 per cent. The transmitter was then heated

[1] I. B. Crandall, loc. cit.

to 100° C. for several hours. After being allowed to cool it was again tested but no change in sensitivity was observable. It is thus reasonable to assume that under ordinary conditions the sensitivity will not change appreciably during the course of several years.

Effect of Temperature and Pressure on Sensitivity.

When a rigid plate was used in place of the flexible rubber diaphragm, *C*, and equalization of the static pressure on the two sides of the diaphragm thereby prevented, measurements with the piston-phone and electrostatic voltmeter showed that the sensitivity of the transmitter changed about 2 per cent. per degree Centigrade at 200 cycles. With the rubber diaphragm, however, within the temperature range of 20 to 40 degrees C. the total change in sensitivity was less than 2 per cent., which is negligible for all practical purposes. The principal reason for this small temperature coefficient lies in the fact that the instrument is constructed almost entirely of the same material. The clamping rings and the diaphragm have nearly the same temperature coefficient of expansion, so that any change in temperature will produce but little change in the tension of the diaphragm. The diaphragm, although thin, cannot assume a temperature very different from that of the frame, for it is separated by such a small distance from the back plate that heat can flow from one to the other nearly as readily as if they were in contact.

If there were no displacement of the rubber diaphragm a change in temperature of 20° C. would produce a difference in pressure on the two sides of the diaphragm equal to 7 per cent. of one atmosphere. It follows, therefore, that a change in atmospheric pressure as great as this will not change the sensitivity of the transmitter by an appreciable amount.

Comparative Sensitivity of the Transmitter.

The mean value of the sensitivity of the transmitter given above is approximately 0.35 millivolt per dyne. A more comprehensible idea of this sensitivity may be obtained from the fact that the male voice in ordinary conversation exerts a pressure of about 10 dynes per sq. cm. at a distance of 3 cm. from the mouth of the speaker.[1] With a three-stage amplifier, thermocouple and galvanometer pressures as low as 0.01 dyne per sq. cm. may be measured. If the tone is produced by some electrical device such as a telephone receiver and the source of current is supplied by an oscillator, an a.c. potentiometer may be used. In this case pressures may be measured which are barely perceptible to the ear.

[1] I. B. Crandall and D. Mac Kenzie, Phys. Rev. (2), XIX, p. 221.

Concluding Remarks.

Little has been said about amplifiers in this paper although the electrostatic transmitter has little practical value unless it is used with an amplifier. Experiments have shown that the transmitter changes but little with time and atmospheric conditions. The amplifier, when properly designed and if the vacuum tubes are carefully chosen, will maintain the same value of amplification for a long period, provided the plate voltage and the filament current are kept at a constant value. An amplifier used in most of the experiments described above did not vary by more than a few per cent. during the course of several months. A combination of electrostatic transmitter and amplifier can thus be used as an absolute phonometer, the readings of which are dependable from day to day.

In the preceding discussion it has already been pointed out that one of the chief merits of the electrostatic transmitter is the fact that it has a very uniform response and so is especially adapted for measuring sounds of complex wave form or for comparing the intensities of tones of different frequencies. However, in some classes of problems it is desirable to have an instrument which is sharply tuned so that it will respond to a tone of one frequency and be unaffected by any other tones that may be present at the same time. If an electrostatic transmitter is connected to a tuned amplifier the output of which goes to a vibration galvanometer, selectivity of a very high order may be obtained and an amplifier of sufficient amplification may be used to give the combination almost any desired sensitivity.

Research Laboratories of the
American Telephone and Telegraph Company,
and Western Electric Company, Inc.

REFLECTION OF X-RAYS FROM ROCK SALT.

By Bergen Davis and W. M. Stempel.

Synopsis.

Reflection of X-rays from Rock-salt Crystals.—By means of the double spectrometer arrangement previously used in studying the reflection from calcite, a narrow beam of nearly homogeneous rays from one crystal was reflected from a second crystal. The two natural cleavage surfaces used were obtained by splitting a good clear specimen. The *rocking curves* are irregular and more than 50 times as wide as corresponding curves for calcite, while the *per cent. reflection at parallelism* of the surfaces was much less than for calcite, being only 10 for 3° grazing angle and 5 for 7°. Polishing the reflecting surfaces increased the curve width somewhat but washing with water restored the surfaces to their original condition. By interposing a third slit between the crystals and moving it across the beam more detailed information was obtained as to the position and character of the imperfections in the crystal surface. Another selected pair of freshly split surfaces gave similar results, except that the per cent. reflection at parallelism was about twice as great.

Imperfections of Rock-salt Crystals.—Compared with calcite, rock-salt crystals are evidently very imperfect. The recent results of W. L. Bragg also prove this. The greater apparent reflectivity observed with rock-salt is due to the fact that its irregular structure reflects a much broader band out of a continuous x-ray spectrum.

In a recent number of the Physical Review (May, 1921) the authors presented some results of an investigation of the reflection of x-rays from calcite. This reflection was investigated by means of a double x-ray spectrometer so arranged that a nearly homogeneous beam of x-rays from the first crystal (A) was allowed to fall on a second crystal (B). Maximum reflection was obtained when the reflecting atomic planes of the two crystals were parallel. On rocking the second crystal about the position of parallelism interesting curves of energy distribution were obtained which were strikingly narrow, the width at half-maximum being as small as 16 seconds of arc in some cases.

A similar investigation has been made of the reflection from the (100) planes of rock-salt. The crystals were mounted on the double spectrometer as shown in Fig. 1. The reader is referred to the original paper for details of the spectrometer and the method of observation.

Two properties in particular of this reflection were investigated. (1) The degree of perfection or imperfection of the crystals as indicated by the width and regularity of the rocking curves. Imperfections in the surface of the crystals or slight local tilting of the reflecting planes have the effect of broadening the rocking curves very much. It was found in the case of calcite, that the more nearly perfect the crystal the nar-

rower and more regular the rocking curves. (2) The ratio of the energy at maximum reflection from the second crystal to the energy of the beam from the first crystal before reflection from the second one. This we call *per cent. reflection.* It is not a true coefficient of reflection, but would probably be the true coefficient for perfect crystals.

Two sets of rock-salt crystals were investigated, which are designated in the tables as crystals No. 1 and crystals No. 2. These crystals were the best that could be obtained from a supply house. They were large, fairly clear and nearly perfect as viewed by the eye. These crystals were split along (100) cleavage planes and mounted on the spectrometer in such position that the two reflecting surfaces were the contiguous planes before splitting. In the case of crystals No. 1 observations were made with the surfaces (*a*) split only, (*b*) polished, (*c*) washed with water.

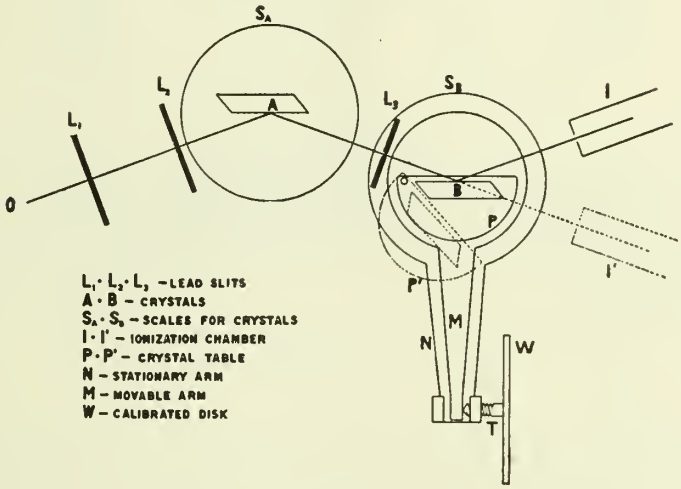


Fig. 1.

Three striking differences are observed between the results for rock-salt and for calcite. (*a*) The rocking curves for rock-salt are many times wider (more than 50 times) than those for calcite. (*b*) The rocking curves were irregular in outline and not symmetrical. (*c*) The per cent. reflection was much less than for calcite.

A third slit L_3 (width .4 mm.) was introduced between the crystals for the purpose of limiting the beam of x-rays to a portion only of the crystal surfaces (see Fig. 1). The types of rocking curves obtained for crystals No. 1, with the slit L_3 so placed as to limit the beam to a region near the center of the crystals are shown in curves Nos. 1, 2 and 3. The widths at half-maxima and the per cent. reflection for the several grazing angles are given in the table.

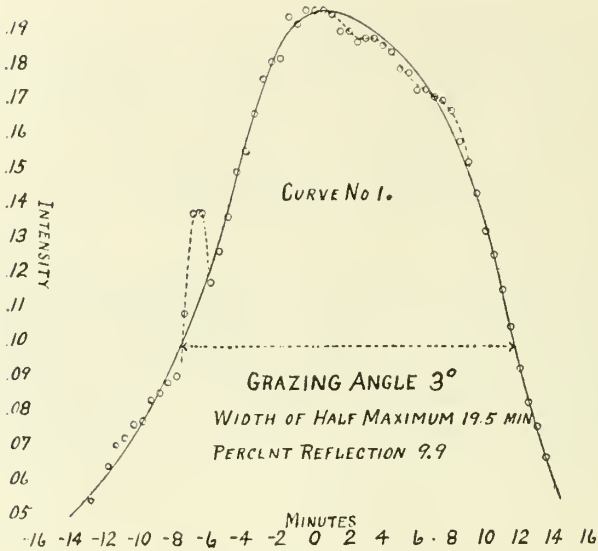


Fig. 2.

These curves all show an irregularity occurring on the same side for all three grazing angles. *However, when the slit was removed so that the beam of x-rays covered nearly the whole of the crystal surfaces the irregularities were ironed out.* The curves were regular in outline but were somewhat unsymmetrical.

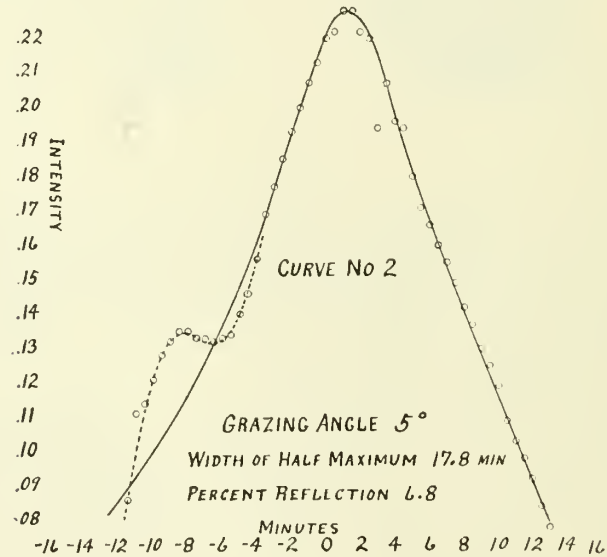


Fig. 3.

These results indicate that the crystals were quite imperfect. To check up these irregular effects, the slit L_3 was progressively moved to different positions across the beam of x-rays. The slit limited the reflection to a new portion of the crystal surfaces for each position. The successive positions of the slit were so adjusted that the regions on the crystals from which the rays were reflected were adjacent to one another. The results are given in the table for three positions A, B and C. The rocking curves obtained, without the irregular humps, are given in Fig. 5.

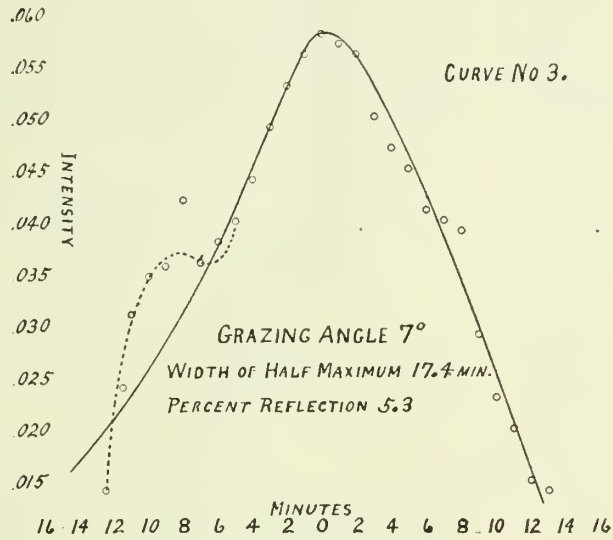


Fig. 4.

The curves A, B and C are given in the order of decreasing glancing angle. The angular position of the curves is displaced but not regularly, as the slit was progressively displaced across the beam. This means that the reflecting elements in the surface of the crystals did not lie in continuous planes, but that in certain regions the reflecting planes were tilted at a small angle to the planes near them. The greatest tilting for the two successive positions A and B was about 14 minutes of arc as indicated by the positions of the curves A and B in the figure. *Had the crystals been perfect these three curves would have been superimposed.*

The above results were obtained with the natural cleavage surfaces of the crystals. Polishing and etching of the surfaces had been observed to produce a great effect on the reflection and width of rocking curves in the case of calcite. The effect of polishing and washing the rock-salt crystal surfaces was investigated and the results are shown at the bottom of the table for crystals No. 1. Observations were made at only one

glancing angle. It will be observed that polishing increased the width of rocking curve to some extent, but that when the surfaces were washed with water to remove the polish they were restored to their original condition. No measurements were made of the per cent. reflection in this instance, as it was not desirable to disturb the setting of the instrument between the processes of polishing and washing.

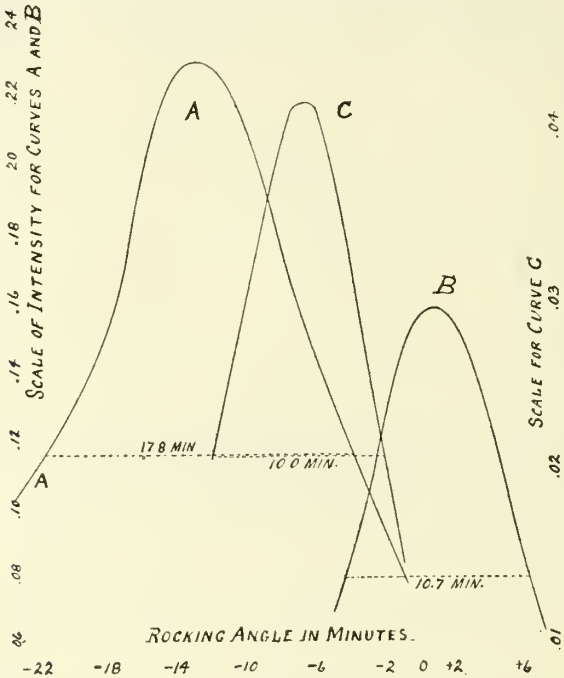


Fig. 5.

To further test this matter of irregular reflection, a new specimen of rock-salt was obtained. This was a large clear piece, in fact, nearly perfect as viewed by the eye. It was found, however, after splitting that the two cleavage surfaces showed small ripples and undulations when examined by reflected light. The crystal was split a number of times until fairly satisfactory surfaces were obtained.

Observations were made with this pair of crystals, (*a*) with freshly split surfaces, (*b*) with the surfaces both polished and washed. The results for three different glancing angles are given in the table for crystals No. 2.

The curve width is somewhat less than that first obtained with crystals No. 1, but is approximately the same as that obtained for No. 1, after the slit L_3 had been once removed and then replaced. It will be noticed

that polishing and washing did not affect the width of rocking curves materially.

The per cent. reflection for this pair of crystals was considerably greater than for the first pair (see column four of the tables).

The decrease in reflection for increase of wave-length was more marked for this pair than for the first pair of crystals.

TABLE I.

ROCK-SALT.

Crystals No. 1 (A_1 and B_1).

Condition of Crystal.	Grazing Angle.	Width at Half-Max.		Per Cent. Reflect.	
With Slit L_3 between Crystals.					
Split only.....		18.7 min.		10.1	
	3°	19.9 min.		9.9	
			19.3 min.		10
		16		8.9	
	5°	17.8		6.8	
			16.9		7.8
	7°		17.4 min.		5.3
Without Slit L_3 between Crystals.					
Split only.....	5°	12.3 min.		9.5	
	7°	11.7		7.6	
	9°	12.5		5.7	
Slit L_3 Moved across X-ray Beam.					
Split only—*A*.....	5°	17.8 min.			
B.....	5°	10			
C.....	5°	10.7			
With Slit L_3 between Crystals.					
Split.....	5°	10.4 min.			
Polished.....	5°	13.7			
Washed.....	5°	10.8			

TABLE II.

Crystals No. 2 (A_2 and B_2).

Condition of Crystal.	Grazing Angle.	Width at Half-Max.	Per Cent. Reflect.
	Slit L_3 between Crystals.		
Split	3°	10.6	24.8
	5°	10.4	15.3
	7°	8.7	13
Surfaces polished and washed	3°	10.9	22.1
	5°	11.5	14.7
	5°	11.1	15.5
	7°	10.9	11.5

These crystals showed so much irregularity in structure, when examined by this method, that but little effect was produced by changing the condition of the reflecting surfaces. In this respect there is a striking contrast between rock-salt and calcite.

The double spectrometer has been applied to crystal reflection by A. H. Compton,[1] and more recently by W. L. Bragg[2] to the investigation of the reflection from imperfect crystals (rock-salt). In this last paper, as an illustration of effect of regular and irregular structure on reflection, Professor Bragg gives two rocking curves. The second crystal in these cases was a thin slab and the curves were taken by transmission. The curve which is given in illustration of regularity of structure is very broad, however. Its breadth is about 30 minutes of arc at half-maximum. This indicates that (*a*) the beam coming from the first crystal to the second was very non-homogeneous, or (*b*) that the second crystal was very irregular in structure, or (*c*) that both of these were true.

Our rocking curves for rock-salt specimens which are manifestly imperfect are more narrow than this one given by Professor Bragg. The experiments previously described for the case of calcite gave rocking curves that are 100 times as narrow as this curve. Calcite approximates to a perfect crystal but is not, of course, completely perfect. This great width of curve given by Professor Bragg would indicate that the crystals were quite imperfect.

Curves Nos. 1, 2 and 3 were all taken with slit L_3 in place. *When*

[1] Proc. Am. Phys. Society, PHYS. REV., July, 1917.

[2] Phil. Mag., March and July, 1921.

slit L_3 was removed so that the rays came from a large portion of the crystal surface, these irregularities were washed out. The curves were regular and smooth, although the crystal was quite imperfect.

It has been noted by a number of experimenters that greater energy is apparently obtained from rock-salt at a first reflection than from calcite. Our results, however, indicate that rock-salt is not so good a reflector as calcite. The calcite *gives a more complete reflection and a much more homogeneous beam of x-rays than rock-salt.* The greater energy observed from rock-salt is due to the fact that at any one position of the crystal the portion ($\Delta\lambda$) selected from the continuous x-ray spectrum is much wider than in the case of calcite.

The results obtained indicate that:

Rock-salt crystals are more apt to be irregular and defective than calcite.

Rock-salt is not so good a reflector of x-rays as calcite.

Rock-salt, owing to irregularities, gives a much less homogeneous beam of x-rays by reflection than calcite.

Phoenix Physical Laboratory,
Columbia University,
December 6, 1921.

SOLUBILITY OF CO_2 AND N_2O IN CERTAIN SOLVENTS.

By William Kunerth.

Synopsis.

Solubility of CO_2 and N_2O in Twelve Solvents, 18° to 36° C.—Since according to the Lewis-Langmuir theory these two gases have similar molecular structures, it is of interest to compare their solubilities in various liquids. In the method adopted, the air was thoroughly removed from the solvent by boiling and then the gas to be tested, having been carefully purified with the help of liquid air, was admitted and shaken up with the solvent until no further solution took place. Observations accurate to better than one per cent. were made for *water, acetone, acetic acid, methyl alcohol, pyridine, ethyl alcohol, benzaldehyde, aniline, amyl acetate, ethylene bromide, isoamyl alcohol, and chloroform.* Taken in this order, the ratio of the solubility of CO_2 to that of N_2O decreases regularly from 1.34 (20°) for water to 0.66 for chloroform. This range of variation is small, and moreover the ratio is nearly constant for each solvent, changing less than one per cent. for six solvents, and not more than three per cent. for the others except chloroform and acetone. Also, the temperature coefficient (ds/sdT) is in most cases nearly the same for the two gases. It is always negative, the solubility decreasing with increasing temperature.

Discussion of Suggested Solubility Relations, for Gases in Liquids.—Raoult's law does not hold for the solubility of gases in liquids. It is also shown that there is little, if any, relation between solubility and the difference between the internal or *cohesion pressures* of solvent and solute. However, the ratio of the solubilities of CO_2 and N_2O varies regularly with the *dielectric constant* of the solvent, and since this constant may be taken as an index of the *polarity* of the solvent and since CO_2 is more active chemically and therefore has stronger polarity than N_2O, this result suggests that polarity may be an important factor in determining the relative solubility of gases in liquids.

Introduction.

In view of the great interest in molecular structure at this time and in view of the possible relation between it and solubility it has seemed of interest and importance to get more complete and more accurate data on certain types of solubility than have hitherto been available.

In the work which is here to be described the solubility of carbon dioxide and of nitrous oxide in twelve different liquids was determined over a range of 18° C. These gases were used because according to recent theories of molecular structure[1] they have the same number and arrangement of electrons. They should therefore exhibit little if any difference in solubility, if the latter depends only on the number and arrangement of electrons. If they do show difference then, according to these theories, it must be due to other properties and the magnitude of the difference should be of interest for any theory of solubility.

[1] Kossell, Ann. der Physik, 49, p. 229 (1916). Lewis, Jour. of Amer. Chem. Soc., 38, p. 762 (1916). Langmuir, Jour. of Amer. Chem. Soc., 41, p. 868 (1919). Thomson, Phil. Mag., 37, p. 419 (1919).

Apparatus.

The apparatus used for this work was very much like that used by McDaniel.[1] The chief part of it is shown in figure 1. It consists of a gas burette *A* (vol. 120 c.c.) which is graduated to 0.5 c.c. and can be read to 0.1 c.c., and an absorption pipette *B* (vol. 31.3 c.c.) connected by a glass capillary *C*. The whole forms one solid piece of glass and is clamped to a wooden frame (not shown in the figure) which is held in an upright position on an iron rod near the burette. With this rod as a pivot the apparatus can be very thoroughly shaken when solution of the gas in the solvent is to take place in the pipette.

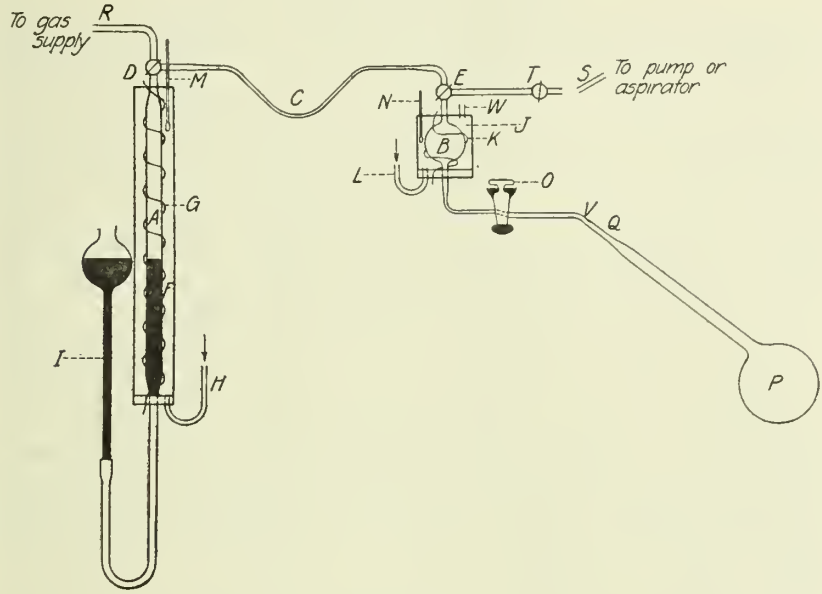


Fig. 1.

At each end of the capillary there is a three-way stopcock (*D*, *E*). The burette is provided with a water jacket *F*, an electric heating coil *G*, and a compressed-air inlet *H*. The reservoir *I* connected with burette *A* by a rubber tube and containing mercury makes it possible to keep the gas in *A* at atmospheric pressure. The pipette is likewise provided with a water jacket *J*, an electric heating coil *K*, and a compressed-air inlet *L*. The coils *G* and *K* are of Chromel *A* wire and either one may be used alone or they may be connected in series. They are so adjusted in length that the resistances are to each other as the respective radiating surfaces of the two water jackets. This insures an equal rate of temperature increase in the two vessels when the coils are in series.

[1] McDaniel, Jour. of Phys. Chem., 15, p. 587 (1911).

Two thermometers *M* and *N* can be read to 0.1° C. and are used to indicate the temperature of the gas in the burette and pipette respectively. *O* is a mercury-seal stopcock, and *P* is a boiler of pyrex glass. *W* is an exit for the air which has been bubbled through the water in *J*. Compressed air is also bubbled through *F* to stir the water and hence assure the same temperature at top and bottom. Stopcock *E* is carefully ground to prevent leakage, and graphite is used as a lubricant on it and also on the mercury-seal stopcock *O*. Grease could be used on neither *E* nor *O* because of the organic solvents used in this work.

Order of Procedure.

In making any determination the burette *A* is filled with mercury except that a few drops of the solvent to be used are put in at the top. After the air has all been pumped out of the tube *RE* and it has been washed out with the pure gas which is to be used in this work, cock *D* is so adjusted as to allow the pure gas to displace the mercury in the burette. Part of the solvent placed in the burette evaporates and thus saturates the gas with the vapor of the solvent. This arrangement makes it unnecessary, as will appear later, to know the vapor pressure of the solvent at any temperature, a quantity which had to be allowed for in Just's work.[1] It is probably for this reason that Just's results on the solubility of CO_2 in liquids do not check very accurately those obtained here. The air is completely removed from the solvent in *P* by boiling for five minutes under reduced pressure and then applying a strong aspirator pump usually for upwards of half an hour more. During this time the solvent in *P* decreases by one fourth or one fifth of its volume. While this is being done *Q* is connected to *S*. Then *Q* is closed by the use of a rubber tube and clip, and forthwith connected to *V*. When the air has next been pumped out of *B* with a good vacuum pump, the boiler *P* is raised above the level of *B* and sufficient air-free solvent is run into *B* by gravity to approximately half fill *B*. To make sure that the last trace of air has been removed from the capillary *C*, this tube is in each case washed out twice with pure gas before a solubility determination is made. A short stub of pressure tubing is used to connect *V* and *Q*. Through this the liquid runs from *P* into *B*. Since this takes only a moment and since the liquids here used have little if any affect on rubber, this proceeding is not objectionable. The solvent is thus at no time exposed to air after once the air has been removed.

The air is then pumped out of the capillary *C* and after stopcock *T* has been closed and *A*, *C*, and *ET* allowed to communicate with each

[1] Just, Z. S. für Phys. Chemie, 37, p. 342 (1901).

other, the height of gas in *A* at atmospheric pressure is carefully read. The mercury reservoir *I* can be raised or lowered to secure atmospheric pressure in *A*. Next *E* is turned so as to bring *B* and *A* into communication, *B* is then shaken to hasten solution and the mercury in *A* rises indicating the volume of gas dissolved. When further shaking causes no more decrease in the volume of the gas in *A* the solution is assumed to be saturated. This takes only a few minutes of thorough agitation of *B*. This apparatus can be shaken more vigorously than that of other investigators and hence solution is hastened. . Since the burette is close to the pivot of the apparatus the mercury in it is little agitated when the pipette is vigorously shaken. In consequence of this there was no emulsion between the mercury and the layer of solvent in the burette above the mercury.

Before solution takes place the temperature is made the same in the two jackets *A* and *B* either by the use of ice water or the electric heating coils. After the reading has again been taken on the burette the temperature is raised simultaneously in both burette and pipette by means of coils *G* and *K*. During this time the shaking is continued, and at the proper time readings are repeated on the burette at intervals of 2° up to 36°. At a temperature much below that of the room it is difficult to keep the two jackets constant and at the same temperature because of radiation.

When the reading for the temperature at 36° has been taken the solvent in *B* is measured in a small graduate calibrated to 0.2 c.c. Dividing the volume of gas which disappears into the solvent by the volume of solvent used gives the solubility at any one temperature. In order to determine the solubility at the other temperatures correction for temperature change has to be applied to the volume of the solvent and also for the expansion of the gas when saturated with the vapor of the solvent as it is in burette *A*. The expansion coefficient of the latter is determined separately in the ordinary way either before or after a regular run. Every determination on solubility is repeated at least once, and recorded results are accurate to within about 1 per cent.

The nitrous oxide for this work was obtained from a steel cylinder of the gas purchased from the S. S. White Dental Company. It was rated as 99.7 per cent. pure, and to further insure its purity it was frozen with ethyl alcohol and liquid air, and while it was in that state all the gases were pumped off. When the frozen nitrous oxide had been thus sublimed it was passed over P_2O_5 and thus freed from possible traces of moisture. Its density was then determined and found to be 1.968 grams per liter at standard temperature and pressure.

With the exception of a short stub of pressure tubing connecting the steel cylinder with the glass system, the entire apparatus containing the purified gas was one piece of solid glass. This insures the continued purity of the gas when it has once been obtained in pure form, and as it is always under pressure a leak would mean a loss of gas rather than a contamination and would be registered on the attached manometer.

The carbon dioxide was made by heating $NaHCO_3$; and after the gas had passed through a long $CaCl_2$ tube to free it from the water, it was treated in the same way as was the nitrous oxide.

The solvents were obtained from standard chemical companies, and tests for boiling point and density were found to be in accord with the tables.

Results.

Table I. shows the solubilities of CO_2 and of N_2O in each one of the twelve liquids used, at intervals of 2° from 18°–36°. The solubility is expressed in c.c. of the gas under existing barometric pressure and at the temperature specified, per c.c. of solvent under the same conditions. It will be noticed that the solubility decreases as the temperature increases, also that the solubilities of CO_2 and of N_2O in any one solvent at a given temperature are very much alike.

Table II. represents the coefficient of temperature change of solubility times 10^2, *i.e.*, $(ds/s \cdot dt)$ at the temperatures indicated. In each case the solubility decreases with increase of temperature.

In Table III. the second column contains the number of molecules of the solvent (M_{solvent}) for each molecule of CO_2 (M_{CO_2}) in a saturated solution at 20° C. The last column contains the corresponding number of molecules of solvent for each molecule of N_2O.

Attempts at the Prediction of Solubility by Raoult's Law.

There are two general principles which have been used in the endeavor to predict solubility and it will be of interest to see how these fare in the interpretation of the foregoing results.

The first one to use Raoult's Law in an attempt to predict solubility seems to have been Dolezalek.[1] As used by him this law means that the partial vapor pressure of one component divided by its vapor pressure when pure and in the liquid state is equal to its number of molecules divided by the total number of molecules in the solution. It is an empirical law giving, for a very limited number of substances,[2] a linear relationship between concentration and vapor pressure.

[1] Dolezalek, Z. S. für Physik Chemie, 64, p. 727 (1908) and p. 1919 (110).

[2] Dolezalek, Z. S. für Physik Chemie, 64, p. 728 (1908).

TABLE I.

	Water.		Acetone.		Acetic Acid.		Pyridine.		Methyl Alcohol.		Ethyl Alcohol.		Benzaldehyde.		Aniline.		Amyl Acetate.		Ethylene Bromide.		Isoamyl Alcohol.		Chloroform.	
	CO_2.	N_2O.	CO_2.	N_2O.	CO_2.	N_2O.	CO_2.	N_2O.	CO_2.	N_2O	CO_2.	N_2O.	CO_2.	N_2O.	CO_2.	N_2O.	CO_2.	N_2O.	CO_2.	N_2O.	CO_2.	N_2O.	CO_2.	N_2O.
18°	....	0.703	....	6.30	5.40	5.00	3.95	....	3.63	3.38	2.95	3.07	3.06	3.23	....	1.50	4.79	5.24	2.32	2.87	....	2.52	3.83	5.70
20	0.900	0.675	6.98	6.03	5.23	4.85	3.85	3.58	3.57	3.32	2.87	2.99	2.98	3.15	1.38	1.48	4.65	5.14	2.27	2.81	1.91	2.47	3.71	5.60
22	0.872	0.638	6.76	5.78	5.07	4.70	3.75	3.50	3.51	3.27	2.80	2.91	2.90	3.07	1.35	1.45	4.55	5.05	2.22	2.75	1.88	2.43	3.60	5.51
24	0.836	0.617	6.55	5.50	4.91	4.55	3.63	3.45	3.44	3.23	2.73	2.85	2.80	3.00	1.32	1.42	4.44	4.93	2.16	2.69	1.85	2.37	3.50	5.26
26	0.800	0.587	6.22	5.21	4.73	4.39	3.53	3.34	3.37	3.19	2.66	2.77	2.73	2.93	1.29	1.40	4.35	4.83	2.12	2.64	1.81	2.32	3.39	5.07
28	0.765	0.561	5.88	4.84	4.57	4.25	3.45	3.25	3.28	3.07	2.58	2.68	2.66	2.85	1.25	1.37	4.24	4.71	2.07	2.58	1.76	2.27	3.26	4.83
30	0.729	0.530	5.49	4.46	4.41	4.11	3.33	3.17	3.19	2.98	2.48	2.61	2.58	2.78	1.22	1.35	4.14	4.60	2.03	2.52	1.72	2.24	3.11	4.57
32	0.693	0.513	5.08	4.07	4.25	3.98	3.25	3.10	3.09	2.88	2.41	2.52	2.52	2.72	1.21	1.32	4.10	4.49	1.97	2.46	1.69	2.19	2.94	4.29
34	0.656	0.478	4.66	3.66	4.12	3.84	3.13	3.02	2.97	....	2.31	2.43	2.46	2.65	1.19	1.31	4.02	4.39	1.92	2.42	1.67	2.16	2.81	4.03
36	....	0.449	....	3.23	4.00	3.75	3.03	2.94	....	....	....	2.33	2.39	2.59	1.17	1.28	....	4.30	1.86	2.37	....	2.12	2.68	3.70

By assuming that gases are completely miscible in liquids, Dolezalek has, however, attempted to apply this law to the computation of the mol-fraction of a gas which under a given pressure is soluble in various solvents.

TABLE II.

Temperature Coefficient of Solubility $\times 10^2$.

Solvents.	Solutes.	18°.	20°.	22°.	24°.	26°.	28°.	30°.	32°.	34°.	36°.
Water	CO_2	1.78	1.88	2.00	2.12	2.23	2.35	2.47	2.58	2.70	2.80
	N_2O	2.03	2.10	2.18	2.27	2.35	2.43	2.52	2.60	2.68	2.76
Acetone	CO_2	0.84	1.27	1.73	2.20	2.66	3.14	3.60	4.13	4.62	5.12
	N_2O	1.50	1.96	2.44	2.94	3.42	3.93	4.40	4.92	5.40	5.90
Acetic acid	CO_2	1.60	1.63	1.65	1.66	1.68	1.70	1.72	1.75	1.76	1.78
	N_2O	1.60	1.62	1.63	1.63	1.64	1.64	1.65	1.65	1.65	1.66
Methyl alcohol	CO_2	0.60	0.76	0.93	1.10	1.26	1.44	1.60	1.77	1.95	2.10
	N_2O	0.40	0.58	0.77	0.97	1.18	1.38	1.57	1.77	1.97	2.17
Pyridine	CO_2	1.28	1.32	1.37	1.41	1.46	1.49	1.53	1.57	1.61	1.66
	N_2O	1.08	1.11	1.14	1.17	1.20	1.23	1.26	1.29	1.32	1.36
Ethyl alcohol	CO_2	1.16	1.23	1.32	1.40	1.48	1.57	1.67	1.74	1.84	1.90
	N_2O	1.16	1.23	1.32	1.40	1.48	1.57	1.67	1.74	1.84	1.90
Benzaldehyde	CO_2	1.32	1.33	1.34	1.34	1.35	1.36	1.37	1.38	1.39	1.39
	N_2O	1.26	1.26	1.25	1.25	1.25	1.26	1.26	1.26	1.26	1.26
Aniline	CO_2	1.12	1.10	1.07	1.05	1.03	1.02	1.00	0.98	0.97	0.95
	N_2O	0.83	0.84	0.85	0.87	0.89	0.90	0.91	0.93	0.94	0.96
Amyl acetate	CO_2	1.35	1.30	1.24	1.19	1.16	1.10	1.03	0.98	0.93	0.88
	N_2O	1.03	1.04	1.05	1.06	1.07	1.09	1.10	1.11	1.12	1.13
Ethylene bromide	CO_2	1.07	1.10	1.13	1.16	1.18	1.21	1.24	1.26	1.29	1.32
	N_2O	1.06	1.06	1.07	1.08	1.09	1.10	1.11	1.12	1.13	1.14
Isoamyl alcohol	CO_2	1.00	0.98	0.97	0.96	0.96	0.95	0.95	0.94	0.94	0.93
	N_2O	1.00	0.98	0.97	0.96	0.96	0.95	0.95	0.94	0.94	0.93
Chloroform	CO_2	1.10	1.30	1.53	1.77	2.00	2.20	2.43	2.66	2.90	3.10
	N_2O	0.66	1.03	1.40	1.80	2.20	2.58	2.98	3.35	3.70	4.07

If Dolezalek's assumption of the validity of Raoult's Law, thus defined, for mixtures of gases in liquids is correct, then obviously the solubility of gases in liquids can be completely predicted if we mean by solubility[1] the mol-fraction of one substance which will be mixed with the other under a given condition of temperature and external pressure. In Dolezalek's paper in which he attempts to test this assumption, he obtains results which are in accord with the theory. However, when the same method is applied to other data wide deviations are found even with the constant he uses.

To see how well we fare in this work in predicting solubilities of gases in liquids by the use of Raoult's Law, let us turn to the first two columns

[1] This use of the word "solubility" is somewhat confusing since it differs from the usual acceptation of the term. This confusion might be reduced by replacing the word "solubility" in its ordinary usage by the word "miscibility."

TABLE III.

	$M_{solvent}$ / M_{CO_2}.	$M_{solvent}$ / M_{N_2O}.
Water	1350	1800
Acetone	46	53
Acetic acid	73	79
Methyl alcohol	155	167
Pyridine	72	77
Ethyl alcohol	131	126
Benzaldehyde	73	69
Aniline	174	162
Amyl acetate	32	29
Ethylene bromide	111	90
Isoamyl alcohol	106	82
Chloroform	74	49

in Table IV. Here are shown the solubilities of CO_2 and of N_2O in terms of mol-fractions in the twelve different solvents used. In the first column of Table V. are shown the solubilities of CO_2 in terms of mol-fractions in twenty different solvents as found by Just. For CO_2 under ordinary conditions the mol-fraction according to Raoult's Law would be 0.0178 = (1/56.3 atm.). This should be the same for all

TABLE IV.

Solvents.	Solubility in Mol-fractions $\times 10^4$ at 20°.		Internal Pressures at 0° C. in Atmospheres.		
	CO_2.	N_2O.	*A.*	*B.*	*C.*
Amyl acetate	283	312	1,500	—	—
Acetone	211	185	2,230	2,600	4,440
Pyridine	129	120	2,460	—	—
Benzaldehyde	125	134	2,440	—	—
Acetic acid	124	115	2,100	5,960	7,140
Chloroform	121	182	2,030	2,430	3,030
Isoamyl alcohol	87	111	2,400	—	—
Ethylene bromide	82	100	2,200	1,980	4,400
Ethyl alcohol	69	72	3,720	3,760	3,120
Methyl alcohol	60	53	4,730	6,360	4,030
Aniline	53	56	2,740	3,300	—
Water	7	5	11,600	17,300	—
CO_2			985	1,510	—
N_2O			980	1,440	—

solvents. From Tables IV. and V. here given we see that the mol-fractions are not what this theory predicts at all and that they are by no means alike. Thus it becomes apparent that this law rarely, if ever, holds for gases dissolved in liquids. This is in accord with the conclusion arrived at by Hildebrand.[1] It means that the procedure of Dolezalek is utterly worthless for predicting solubility of gases in liquids.

TABLE V.

Solvents.	Solubility of CO_2 in Mol-fractions $\times 10^4$ at 20°.	Internal Pressures at 0° C. in Atmospheres.		
		A.	*B.*	*C.*
Amyl acetate	270	1,500	—	—
Acetone	209	2,230	2,600	4,440
Pyridine	129	2,460	—	—
Benzaldehyde	128	2,440	—	—
Ethylene chloride	125	2,070	2,730	4,500
Chloroform	123	2,030	2,430	3,030
Acetic acid	121	2,100	5,960	7,140
Nitrobenzene	113	2,340	—	—
Toluene	107	1,710	2,210	3,570
Meta xylene	102	1,670	2,100	—
Carbon tetrachloride	100	1,685	2,030	3,220
Benzene	91	1,870	2,240	3,900
Ethylene bromide	82	2,200	1,980	4,400
Propyl alcohol	77	2,970	3,020	2,480
Methyl alcohol	71	4,730	6,360	4,030
Ethyl alcohol	70	3,720	3,760	3,120
O — toluidine	66	2,280	—	—
Aniline	55	2,740	3,300	—
Carbon disulphide	22	3,000	3,220	3,800
Water	7	11,600	17,300	—

ATTEMPTS AT THE PREDICTION OF SOLUBILITY FROM COHESION PRESSURES.

The real problem of predicting solubility comes where the components are not completely miscible. The method here to be discussed has been used by Traube,[2] Walden,[2] Hildebrand,[2] and Bradford,[2] and consists essentially in the assumption that two substances will be more nearly soluble in one another in proportion as the internal pressures (Laplace's cohesion constants) of the two substances approach one another. The fundamental idea underlying this theory appears to be that if two

[1] Hildebrand, Jour. of Amer. Chem. Soc., 38, p. 1454 (1916).

[2] Traube, Verh. der d. Physik Gesell, 10, p. 880 (1908). Walden, Z. S. fur Phys. Chemie, 66, p. 409 (1909). Hildebrand, Jour. of Amer. Chem. Soc., 38, p. 1452 (1916). Bradford, Phil. Mag., 38, p. 696 (1919).

substances A and B have the same cohesion pressures when in the liquid state, then the molecules of substance A will exert the same sort of forces upon the molecules of substance B as the molecules of A (or of B) exert upon one another. In other words, if A's molecules have a certain attraction for one another as measured by cohesion pressure and B's molecules have the same attraction, then the two substances will readily mix, but if the cohesion pressure of either one is greater than that of the other then the one will draw itself away from the other just as would be expected if there were no such thing as selectivity among molecular forces. This idea is perhaps most definitely expressed in an equation set up by Bradford and written in the form

$$f = \frac{M_A^2}{r_A^4} - \frac{2M_AM_B}{r_{AB}^4} + \frac{M_B^2}{r_B^4}.$$

The f in this expression is what he calls the force opposing solution, the term M_A^2/r_A^4 is the term which in his theory is proportional to the internal pressure of substance A, whereas the term M_B^2/r_B^4 is proportional to the internal pressure of substance B. The attraction between molecules of substance A is assumed to be electrical in origin and the term M in Bradford's theory is what he calls the electrical "moments of the atomic doublets in each molecule." He assumes, following the proofs given by J. J. Thomson[1] and by Sutherland,[2] that with such forces the molecular attraction will be inversely proportional to the fourth power of the distance between molecules. Hence he gets the form of the cohesion term M^2/r^4. The force drawing molecules A and B together is then of the form $2M_AM_B/r_{AB}^4$, so that the force opposing solution is the difference between this term and the sum of the other two terms which express the cohesion of the molecules for each other respectively.

From this point of view we should be able to calculate the value of the solubility of one component in another if we have given their internal pressures. These I have calculated by three different methods and listed under headings A, B, and C in Tables IV. and V. for the solvents found in column one in each case. Under A are found the internal pressures obtained by Stefan's method,[3] under B the Laplacian cohesion constant obtained from the expression $K = a(v_1/v_2)^2$, and under C are the internal pressures obtained by use of the expression[4] $K = \alpha T/\beta$ where α is the expansion and β the compressibility coefficient. The data required for the calculation of internal pressures were obtained from the Landolt-Börnstein Tables.

[1] Thomson, Phil. Mag., 27, p. 757 (1914).

[2] Sutherland, Phil. Mag. (5), 39, p. 1 (1895).

[3] Stefan, Wied. Ann., 29, p. 655 (1886).

[4] Kleeman, Kinetic Theory of Gases and Liquids, p. 71.

To show how the theory of internal pressures works out when applied to the data here obtained we need to refer again to Table IV. where the solvents are arranged in decreasing order of the solubility of CO_2, but the order would be very nearly the same if arranged according to N_2O. The cohesion pressure theory requires that the solubility should decrease as the difference of internal pressures between solvent and solute increases. The fact that the solubilities are those at 20° C. and the internal pressures are at 0° C., makes little if any difference in the relative order of solvent and internal pressure. It will be evident from Table IV. that there is no correlation there which is sufficiently good even as evidence that this theory is in its main features correct. It will also be noticed that as far as the reliability of the theory is concerned it is immaterial which of the three methods of calculating internal pressures is used. It is true that some of the solvents are probably associated. But the situation is not improved even by omitting entirely those solvents which we feel confident are associated.

Bradford has used this method for the prediction of solubility with some apparent success, as is shown in the table he cites. But the agreement which is there shown is accidental, I think, and due to the relatively few cases chosen.

Hildebrand [1] also sets up a similar table and draws the conclusion that Bradford does. In my opinion a critical study of his table yields no evidence which justifies a conclusion of this kind, and when this table is extended to more solvents as is done in Table V. above, where the solubilities are those by Just on CO_2 and are listed in decreasing order of magnitude, the conclusion Hildebrand draws is very obviously not warranted. When a comparison is made with the theory the departures will be seen to be just as great as in Table IV. So far, therefore, as these data are concerned, this method must be considered practically useless.

Again it should follow from the point of view of this theory that:

1. Substances which have the same internal pressures should all be completely miscible.

2. All substances which are completely miscible should have the same internal pressures.

3. The order of miscibility should be the order of difference in internal pressures.

As to the third point we note from the tables given above that it does not hold at all.

Under the second point should be mentioned many combinations of

[1] Hildebrand, Jour. of Amer. Chem. Soc., 38, p. 1467 (1916).

non-associated liquids miscible in all proportions, the internal pressures of whose components are widely different. These are not in accordance with the theory. Among these may be mentioned ether and benzaldehyde, ether and chloroform, ethylene bromide and ether, ethylene chloride and ether, carbon disulphide and ether. According to the theory these should not be completely miscible. It should be said that Hildebrand also recognizes a difficulty of this sort.

Under the first point above mentioned there are only a few cases to be considered because very few substances have the same or very nearly the same internal pressure. The combinations cited by Hildebrand should be noted. They are benzene and carbon tetrachloride, benzene and chlorobenzene, benzene and chloroform, benzene and ethylene chloride, chlorobenzene and toluene. They have nearly equal internal pressures and are miscible in all proportions. But methyl alcohol should be completely miscible in carbon disulphide, for according to one method at least their internal pressures are nearly alike. The polarity of methyl alcohol is given as the cause of this discrepancy. This suggests that polarity as a factor in solubility may be worthy of further study. But the conclusion of the studies in this field would appear to be that present theories of miscibility, though perhaps of some little value as indices, can scarcely be said to have gained any very notable successes.

Polarity.

If we now turn to Table VI. where are listed the ratios of solubilities of CO_2 to N_2O in the twelve solvents here used, it seems worthy

Table VI.

Ratio of Solubility of CO_2 to that of N_2O.

Solvents.	18°.	20°.	22°.	24°.	26°.	28°.	30°.	32°.	34°.	36°.
Water	....	1.333	1.366	1.354	1.363	1.364	1.372	1.350	1.370	....
Acetone	....	1.157	1.170	1.191	1.194	1.215	1.230	1.248	1.272	....
Acetic acid	1.080	1.078	1.078	1.078	1.076	1.075	1.072	1.067	1.072	1.066
Methyl alcohol	1.073	1.075	1.073	1.065	1.056	1.068	1.070	1.072	....	....
Pyridine	....	1.075	1.070	1.052	1.057	1.060	1.050	1.048	1.035	1.030
Ethyl alcohol	0.961	0.960	0.963	0.958	0.960	0.963	0.950	0.957	0.950	....
Benzaldehyde	0.048	0.946	0.945	0.933	0.932	0.933	0.928	0.927	0.928	0.923
Aniline	....	0.932	0.931	0.930	0.922	0.912	0.904	0.917	0.908	0.914
Amyl acetate	0.914	0.905	0.902	0.902	0.900	0.901	0.901	0.913	0.916	....
Ethylene bromide	0.808	0.807	0.807	0.803	0.803	0.803	0.805	0.801	0.793	0.785
Isoamyl alcohol	....	0.773	0.774	0.781	0.780	0.776	0.768	0.772	0.773	....
Chloroform	0.672	0.663	0.653	0.666	0.668	0.674	0.680	0.685	0.697	0.724

of note that CO_2, which is considered more polar than N_2O, is also in general more soluble than N_2O in the solvents considered polar, namely: water, acetone, acetic acid, methyl and ethyl alcohol. CO_2 and N_2O are so completely alike in so many ways that it is perhaps difficult to differentiate them on the basis of polarity. The dielectric constant which is usually considered a criterion of polarity is the same in the two cases, but chemical reactivity is also a sign of polarity and in this respect CO_2 differs from N_2O, being more active than the latter. For the solvents here mentioned we can apply the criterion of the dielectric constant and order their polarities on the basis of this property.

At present there exists little definite quantitative data on the effect of polar substances upon each other and upon non-polar substances in their neighborhood; but so far as the present table goes its indications are that the solubility of gases in liquids is connected with polarity rather than with Raoult's law or with internal pressures.

The indications of the present work then are that the most hopeful lines of attack for the problem of the prediction of solubility must be looked for in the study of chemical properties rather than of physical properties such as internal pressures.

In conclusion the writer wishes to acknowledge his indebtedness to Prof. R. A. Millikan for suggesting the subject, for his kindly interest in this work, and for his continuous friendly advice and help, and to Prof. A. J. Dempster for occasional assistance.

RYERSON PHYSICAL LABORATORY,
CHICAGO, ILL.,
September -, 1921.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE NEW YORK MEETING, FEBRUARY 25, 1922.

THE 113th meeting of The American Physical Society was held in the lecture theater of Schermerhorn Hall, Columbia University, New York City, on Saturday, February 25, 1922. There were morning and afternoon sessions with an attendance of about one hundred and seventy-five members and visitors. The president of the Society, Theodore Lyman, presided at both sessions.

There was a meeting of the Council on the evening of Friday, February 24, 1922, at the Columbia University Club. The following elections were made: *elected to Fellowship*, Worth Huff Rodebush; *transferred from Membership to Fellowship*, Walter F. Colby and Orin F. Tugman; *elected to Membership*, William C. Beller, William B. Bohanon, G. Breit, August Concilio, James Cork, Chester S. Cutshall, Pasquale J. Federico, H. C. Frank, W. H. Fulweiler, Elmer Hutchisson, Albert Kalin, Elizabeth A. Mitchell, Pierre LeCompte du Nouy, Chas. W. Prine, J. Howard Rowan, George W. Schneider, George W. Sherman, Jr., Khimji B. Thakkur, J. R. Tolmie, Dare Abernathy Wells, William R. Westhafer and P. B. Winn.

The following program of twenty-eight papers was presented, three, Nos. 3, 5, and 9, being read by title:

1. The Rigidity and Viscosity of Ice. C. D. HAIGIS, presented by A. W. Duff.
2. The Measurement of Intravenous Temperatures. HARRY CLARK.
3. The Effect of Nascent Hydrogen on Hard Steel Magnets. JOHN COULSON.
4. Magnetostriction with Small Magnetizing Fields. JOHN R. HOBBIE, JR.
5. Some Optical and Electrical Properties of Rochelle Salt. J. VALASEK.
6. The Spectrum of Fluorine. HENRY G. GALE.
7. Improvement in the Determination of the Radium Content of Low-Grade Radium Barium Salts. VICTOR F. HESS and ELIZABETH E. DAMON.
8. On the Operating Characteristics of the Audion. LYNDE P. WHEELER.
9. The Effect of Crystal Structure upon Photoelectrical Sensitivity. W. W. COBLENTZ.
10. New Evidence Regarding the Interpretation of Critical Potentials in Hydrogen. P. S. OLMSTEAD.

11. Low Voltage Arcs in Diatomic Gases and the Effect of Dissociation in a Tungsten Furnace. O. S. DUFFENDACK, introduced by K. T. Compton.

12. Magnetic Control of Thermionic Emission from a Straight Wire by Current in the Wire. ALBERT W. HULL.

13. A Test of Theories of Cumulative Ionization. K. T. COMPTON.

14. The Scattering of Electrons by Aluminum. C. DAVISSON and C. H. KUNSMAN.

15. The Ratio of the Two Elementary Charges. F. W. LOOMIS.

16. Ionization and Radiation Potentials and the Size of the Atom. BERGEN DAVIS.

17. On the Spectra of X-Rays of Short Wave-Lengths. WILLIAM DUANE and K. C. MAZUMDER.

18. The Crystal Structure of Silver-Palladium and Silver-Gold Alloys. L. W. MCKEEHAN.

19. Precision Measurement of Crystals. WHEELER P. DAVEY.

20. A Spectrographic Study of Ultraviolet Fluorescence Excited by X-Rays. J. O. PERRINE.

21. The Grating Space of Mica and the Intensities of the Spectral Orders. BERGEN DAVIS and H. M. TERRILL.

22. A New Type of Bumstead Electrometer and Accessory Apparatus. HARRY CLARK.

23. Dynamic Characteristics of Helium Arcs. FABIAN M. KANNENSTINE.

24. The Joule Effect in Steel Rods at Different Drawing Temperatures. S. R. WILLIAMS and O. KOPPIUS.

25. Effects Obtained with an Alternating Current Sent Through a Capillary Electrometer. R. D. KLEEMAN and D. T. SIMMONDS.

26. Note on the Formation of Negative Ions in a Gas. R. D. KLEEMAN.

27. Note on X-Ray Spectra. WILLIAM DUANE and R. A. PATTERSON.

28. The Electric Fields of Some Constant Electromagnetic Systems in Motion. S. J. BARNETT.

The abstracts of the papers in the above program, with corresponding numbers, are given on the following pages.

DAYTON C. MILLER,
Secretary.

1. THE VISCOSITY AND RIGIDITY OF ICE.

BY C. D. HARGIS.

PREVIOUS work, principally by Hess in 1902, showed that the coefficient of viscosity of ice increases with the time that the shearing stress has been acting. He found for the coefficient a value of $.6 \times 10^{11}$ after 15 seconds and a value of 120×10^{11} after 28,000 seconds. Using these results he showed that the slow motion of a glacier can be accounted for.

In the present work the coefficient of viscosity and the rigidity were determined kinetically under conditions where the time of shear was a fraction

of a second. A cylinder of ice was frozen in a brass tube, withdrawn, and mounted as a torsional pendulum, the upper end being frozen solidly to a support. The lower end was free and carried a mass whose moment of inertia was 5.67×10^5 gm. cm.^{2} and in addition a small mirror. A ray of light from an arc light was reflected by the mirror through lenses onto a moving film which also had seconds intervals recorded by a small filament flashing at intervals of a second. The equation giving the motion of the rod is of the form

$$K \frac{d^2\theta}{dt^2} + L \frac{d\theta}{dt} + M\theta = 0,$$

where

$$L = \eta \frac{\pi r^4}{2L} \qquad \text{and} \qquad M = n \frac{\pi r^4}{2L}.$$

This equation integrated gives the coefficient of viscosity and the rigidity in terms of the logarithmic decrement, period, length, radius, and moment of inertia.

A pendulum 226 cm. in length, of period .468 second and radius .863 cm. gave for the coefficient of viscosity 6.12×10^9 and for the rigidity 2.66×10^{10}. Another pendulum of length 111 cm., period .286 second and radius .802 cm. gave for the coefficient of viscosity 3.8×10^9 and for the rigidity a value of 2.91×10^{10}. The average value of the rigidity from eight observations was 2.82×10^{10} and the coefficient of viscosity varied from 3.8×10^9 for a period of .286 second to 6.33×10^9 for a period of .448 second. The mean deviation of the eight observations of rigidity from the value 2.82×10^{10} was $.15 \times 10^{10}$.

Worcester Polytechnic Institute.

2. The Measurement of Intravenous Temperatures.

By Harry Clark.

A copper-constantan thermocouple is sealed inside a steel tube, which is small enough in diameter to pass freely through a hypodermic needle. It can thus be placed in a blood vessel, the flow of blood between the tube and the needle showing when the vessel has been properly located. Temperatures are read by a galvanometer-deflection method. The second thermal junction is kept at $37 \pm 0.001°$ C. by means of an electrical thermostat which operates without stirring device or relay, and from which the troubles caused by fouling of the mercury contact have been entirely eliminated. Experiments on animals show that the blood temperature remains constant to within perhaps 0.01° C. over considerable lengths of time. Clinical experiments will be begun shortly to determine the degree of importance to be attached to such measurements.

The Rockefeller Institute of Medical Research,
New York City.

3. The Effect of Nascent Hydrogen on Hard Steel Magnets.

By John Coulson.

Investigations having proven that steel absorbs hydrogen at ordinary temperatures it was considered probable that the "aging" of *permanent magnets* was due primarily to the action of slowly absorbed hydrogen. Bar magnets of "Special Alloy Magnet Steel" and high carbon steels were exposed to the action of electrolytic hydrogen while serving as kathode in an electrolyte of 25 per cent. H_2SO_4. Results of observation are given in table and in curves showing the decrease in magnetic moment as a function of the time of exposure.

Well *seasoned* magnets of drill rod, quenched glass-hard, underwent a further decrease in moment of 14 per cent. on exposure to the hydrogen. The moment of similar magnets of spring steel and special magnet steel experienced a precipitous drop in the course of the electrolytic treatment, which was not in evidence with magnets of drill rod. For magnets of spring steel this sudden drop occurred after 20 or 30 minutes' exposure, and amounted to about 5 per cent. For the special magnet steel it occurred after a few minutes, and in some cases had a magnitude of 19 per cent. Before and after this sudden transition the rate of change in moment was only a fraction of one per cent.

Exposing the magnets to the electrolytically evolved hydrogen in heated electrolyte accelerated this aging process. At 60° C. the magnetic moment reached stability in an hour or less. Hammering the magnet at this stage had little or no effect on its moment. The effect usually is about one part in 1600.

Photographs of cold-rolled steel broken under stress show the depth to which the electrolytic hydrogen penetrated for 40 seconds' exposure.

University of Pittsburgh.

4. Magnetostriction with Small Magnetizing Fields.

By John R. Hobbie, Jr.

Piezo-electric Method of Measuring Extremely Small Magnetostriction Effects.—In this method, suggested by Pupin, the wire to be studied is surrounded by a solenoid through which an alternating current of known strength and frequency is sent, and the vibrations set up in the wire are transmitted to a piezo-electric crystal and the resulting electric charge is amplified and measured.

For elongations down to 2×10^{-9} the wire was hung directly from a *quartz crystal.* To measure the charge produced by a given magnetizing current, an electromotive force of the same frequency, and adjusted to the proper phase by means of a *Pupin wave balance*, was fed to the amplifier through a vacuum tube in parallel with the one connected to the crystal, and the potential was varied until the note produced by the crystal was balanced out. The force corresponding to a given charge was determined with the aid of a condenser, one plate of which was suspended from the crystal.

By using the torsion of a *Rochelle salt crystal* the sensitiveness of the method was extended to 2×10^{-11}, and by tuning both the crystal and wire to resonance

with the frequency used, a sensitiveness of 3×10^{-12} was reached. The last two arrangements were calibrated in absolute units by comparison of the results with those obtained with quartz. The smallest change previously measured was about 10^{-8}.

Magnetostriction with Small Magnetizing Fields.—An *iron* wire and a *nickel* wire were studied. In each case the curve for magnetostriction as a function of the field is nearly linear, but slightly concave downward in its lower portion, and apparently passes through the origin. For fields of 1, 0.05 and 0.002 gauss, the ratio of magnetostriction to field strength is respectively 3, 2.4 and 4×10^{-9} for iron, and 2, 1 and 3×10^{-9} for nickel. The *probable* error is from 7 to 10 per cent.

Columbia University.

5. Some Optical and Electrical Properties of Rochelle Salt.

By J. Valasek.

The three main indices of Rochelle salt have been measured for several wave-lengths in the visible region and for temperatures between $-70°$ C. and $+40°$ C. Their variation with temperature was approximately linear throughout the range although the dielectric and piezoelectric constants both undergo an increase of several hundred per cent. in the temperature interval of $-25°$ to $-15°$ C. and a corresponding decrease in the interval of $+20°$ to $+30°$ C. Hence the doublets responsible for the large piezoelectric and dielectric action of Rochelle salt have a low natural frequency somewhere well below the immediate infra-red.

In order to ascertain whether the large temperature coefficient of the indices of refraction was, as usual, due to a changing density, the coefficients of expansion were measured in the three main directions by the Fizeau method. On applying the Lorentz-Lorentz formula,

$$\frac{n^2 - 1}{n^2 - \dfrac{\alpha - 1}{\alpha}} = \alpha C\rho,$$

the above view was confirmed but the values of α necessary to fit the observations were much smaller than the value of 1/3 for a uniform distribution of charges. The values differed for the three indices but were always between zero and one-tenth. In general a small α means that the force on the charges which have an appreciable effect in dispersion is nearly equal to the electric vector of the incident wave and hence a formula of the Sellmeier type should represent the dispersion.

Preliminary observations indicate the existence of a "real" pyroelectric effect in Rochelle salt. Below 0° C. the natural polarization of the crystal increases and causes a charge to appear on the faces of a plate cut normal to the ă axis when it is heated. Above 0° C. the opposite variation of charge

takes place. Since the dilatations are monotonically increasing while the pyroelectric charge reverses in sign, there is evidence here of a real pyroelectric effect the existence of which is doubted by Voigt from observations made on other crystals.

UNIVERSITY OF MINNESOTA,
February 8, 1922.

6. THE SPECTRUM OF FLUORINE.

BY HENRY G. GALE.

FLUORINE has been generated with the apparatus described by Smythe (Astrophysical Journal, 44, 133, 1921). Heavy copper electrodes tipped with gold, were inserted through ground joints into a bulb of about 500 c.c. capacity, and the spectrum photographed through a fluorite window at atmospheric pressure. The spectrum has also been photographed at reduced pressures, using an ordinary vacuum tube with copper electrodes. A concave grating of 1.5 meters' radius was used, the ruled surface, 10 cm. by 4 cm., having 600 lines per mm. The lines are of fair quality at atmospheric pressure, and are very sharp at a pressure of about 6 mm. to 10 mm. Measurements have been made on 52 lines between λ 3470 and λ 7800. Except 7 lines to the red of λ 7400, all of these are included in the tables of Exner and Haschek, Porlezza, Lunt or Moissan. With a powerful spark, 15 additional lines appear in the red and orange regions. The wave-lengths are accurate to about .05 Å. There are a number of interesting triplets and doublets.

UNIVERSITY OF CHICAGO.

7. IMPROVEMENT IN THE DETERMINATION OF THE RADIUM CONTENT OF LOW-GRADE RADIUM BARIUM SALTS.

BY VICTOR F. HESS AND ELIZABETH E. DAMON.

THE present gamma-ray methods of determining the radium content of low-grade radium salts are rather inaccurate due to the varying influence of the absorption of the salt itself. Likewise the emanation method gives a lesser degree of accuracy because repeated dilutions of the liquid are necessary.

One of the authors has devised a portable string electrometer (electric capacity 1 cm.) which is very sensitive. A hollow curved tin plate container (10 cm. high, 2 cm. thick) was filled with inactive barium salts and placed at a distance of 30 cm. (the radius of curvature of the tin plate container) from the center of the electrometer. A small radium tube (0.87 mg.) was imbedded in the salt at different positions throughout and the average of these readings agreed with the average of two readings taken with the radium tube fixed on the outside wall of the container, front and back, within one per cent.

The container was then filled with another salt, but radioactive. Readings were taken with and without the standard attached and the amount of radium computed. Knowing the quantity of salt in the container results may be

expressed in mg. of radium per kg. Equilibrium values may be calculated from two successive readings.

A concrete example may illustrate: a sample dissolved in hydrochloric acid and residues decomposed again gave, measured by the emanation method, 1.05 mg. Ra/kg. Sample of the same material dissolved in concentrated sulfuric acid gave 1.11 mg./kg. (emanation method). The gamma-ray method described above gave 1.10 mg./kg. This method has the advantage of greater accuracy and requires much less time.

U. S. Radium Corporation, Orange, N. J.

8. On the Operating Characteristics of the Audion.

By Lynde P. Wheeler.

In order to predetermine the behavior of the three-element thermionic vacuum tube when functioning in a given circuit, it is important to have a grid voltage-plate current characteristic for the operating conditions. Such curves are usually obtained experimentally for each value of the contemplated impedance of the plate circuit.

It is shown in this paper how these operating characteristics can be computed from the ordinary static characteristics of the tube which are measured with negligible impedance in the plate circuit. Only the case where the external impedance is a pure resistance is treated. The extension of the results to include reactance can be readily made.

The expression by means of which such computations can be made is obtained by transforming the parabolic equation for the plate current in terms of the grid and plate voltages into one in terms of the external and internal resistances of the plate circuit. When this is accomplished, it appears that the operating characteristic can be obtained from the simple static characteristic of the tube without external resistance by multiplying each ordinate of the latter by a numerical factor whose magnitude depends only on the ratio of the external and internal resistances. This factor is a constant for a steady, and very approximately so for an A.C., e.m.f. applied in the grid circuit. Its magnitude varies from unity when the external resistance is zero to zero when it is infinite.

It is further shown how an expression for the A.C. component of the plate current can be obtained when the characteristic is parabolic. From the form of this expression it is seen that in addition to producing distortion, the curvature of the characteristic changes the effective resistance of the plate circuit from that which obtains for a linear characteristic. The factor which determines the magnitude of this change also depends only on the ratio of the external and internal resistances, and varies from unity when the external resistance is zero to two when it is infinite. Thus the common statement that the effect of curvature is to introduce harmonics but not to change the magnitude of the fundamental component of the plate current must be modified.

Yale University.

9. The Effect of Crystal Structure upon Photoelectrical Sensitivity.

By W. W. Coblentz.

Silver sulphide, Ag_2S, as a mineral, occurs in two crystal forms: *Argentite* which is isometric and *Acanthite* which is orthorhombic. Both minerals are photoelectrically sensitive, and hence form interesting material for studying the effect of crystal structure upon photosensitivity.

Argentite.—Applying spectral radiation stimuli of equal energy, it is found that, at 20° C., argentite reacts slightly to radiations of wave lengths 0.6 μ to 1.1 μ, followed by a sharp, fairly symmetrical maximum at 1.35 μ. At low temperatures (− 100° C.) this maximum shifts to the short wave-lengths, − 1.1 μ. At all temperatures the spectrophotoelectrical reaction appears to be positive, *i.e.*, the resistance decreases when the mineral is exposed to radiation. The general outline of the curve exhibiting the spectrophotoelectrical reaction is fairly uniform for different samples.

Acanthite.—The electrical reaction of acanthite differs from that of argentite in that the radiation stimulus appears to induce a photo-negative response (increase in resistance, or counter e.m.f.) which is superposed upon the photo-positive response usually observed in substances exhibiting photosensitivity. Moreover, at 20° C. the photoelectrical reaction is high for radiations of wave-lengths 0.6 μ to 1.1 μ, followed by an unsymmetrical maximum at 1.4 μ. At low temperatures the sensitivity curve is symmetrical with the maximum shifted to 1.2 μ. The general outline of the curve exhibiting the spectro-photoelectrical reaction differs greatly for different samples. Since the samples examined are usually aggregates of crystals, which are no doubt irregularly arranged, it would appear that, in the orthorhombic crystal, the inequality of the axes has a marked effect upon spectro-photoelectrical conduction.

Washington, D. C.,
February 4, 1922.

10. New Evidence Regarding the Interpretation of Critical Potentials in Hydrogen.

By P. S. Olmstead.

Method of Producing Atomic Hydrogen.—A close grid of tungsten wires was introduced close to the gauze in an ionization tube of the Lenard type. By heating this grid to incandescence, a certain amount of atomic hydrogen should be produced by dissociation. Ionization or radiation at critical potentials of *atomic* hydrogen should be greater, relatively to effects due to molecular hydrogen, if this grid is hot.

Method of Distinguishing between Effects of Radiation and Ionization.—The receiving electrode could be either (1) a wire point of very small area, or, (2) a disk of large area. The former is relatively insensitive to effects of radiation since little radiant energy strikes it.

Critical Potentials of Hydrogen.—Thus, it is shown that 13.5 volts is the

ionizing potential of the *hydrogen atom.* There are two critical potentials near 11 volts; *ionization of the molecule* (probably without dissociation) at about 11.5 volts, and a weaker effect, ascribed to radiation from the atom, at about 10.2 volts. The strongest effect, dissociation of the molecule, and ionization of one of its parts, is put at 16 volts. Accurate experiments and special averaging methods were necessary, since the amount of atomic hydrogen produced by the incandescent grid was relatively small.

PRINCETON UNIVERSITY.

11. LOW-VOLTAGE ARCS IN DIATOMIC GASES AND THE EFFECT OF DISSOCIATION IN A TUNGSTEN FURNACE.

BY O. S. DUFFENDACK.

Meaning of an Arc.—When the space charge surrounding an incandescent cathode is neutralized by positive ions, the arc strikes and a redistribution of electric intensity, giving a large drop in potential near the cathode, results. This enables an electron to ionize a molecule at its first impact, and so an arc can be maintained at the ionizing potential, or lower if the molecules are already partially ionized.

Average Breaking Potentials in Hydrogen and Nitrogen.—In hydrogen and nitrogen the average potentials of the breaks of arcs between a filament and a plate were 16.35 and 16.16 volts, respectively, which are within the range of ionizing potentials of the molecules reported for these substances. As Bohr's theory puts the ionizing potential of the hydrogen atom at 13.52 volts and the radiating potential at 10.14 volts, it seemed that it should be possible to maintain the arc at these voltages if there were sufficient monatomic hydrogen present.

Arcs in Monatomic Hydrogen.—When a tungsten furnace was employed, giving from 27 per cent. to 90 per cent. dissociation at 2000° K. to 2500° K., the arc was maintained to 14 volts and the curves for the thermionic currents show sharp discontinuities at about 10, 14, and 16.5 volts.

PRINCETON UNIVERSITY.

12. MAGNETIC CONTROL OF THERMIONIC EMISSION FROM A STRAIGHT WIRE BY CURRENT IN THE WIRE.

BY ALBERT W. HULL.

Mathematical analysis of the motion of electrons from a straight wire to a concentric cylinder shows that the electrons will reach the cylinder if the ratio of potential difference to current in the wire is greater than a critical value, and will fail to reach it if the ratio is less than that value.

The critical value of current is

$$I = \frac{E^{\frac{1}{2}}}{\sqrt{2\frac{e}{m}\log\frac{R}{r_0}}},$$

where E is the potential difference and R and r_0 the radii of cylinder and wire.

This relation has been verified by experiments with tungsten-wire filaments up to 2.5 mm. diameter, using the heating current as control current. The results are shown by volt-ampere curves for constant-filament current, and oscillograms for alternating filament current.

For a tungsten filament of diameter d cm. at 2500° K., heated by direct current, the critical voltage is

$$E = 5310d^3 \left(\log_{10} \frac{R}{r_0} \right)^2 \text{ volts.}$$

This is negligible for a 1/4 mm. (10 mil) filament, but is approximately 10,000 volts for a 5 mm. filament in a 10 cm. cylinder, and nearly 100,000 volts for a 1 cm. filament.

RESEARCH LABORATORY,
GENERAL ELECTRIC CO.,
SCHENECTADY, N. Y.,
February 8, 1922.

13. A TEST OF THEORIES OF CUMULATIVE IONIZATION.

BY K. T. COMPTON.

Current Preceding Striking of Arc.—Using the equation

$$n/n_0 = 1/(1 - 4\sqrt{3680MP_0})$$

for the current n, in terms of the current n_0 if there were no ionization, the molecular weight M of the gas and the probability P_0 of partial ionization of a molecule, values of P_0 were calculated for ionization in helium at various pressures, currents and voltages.

Ionization by Successive Impacts.—These values of P are substituted in the equation derived by the writer for ionization by successive impacts to test its adequacy. The conclusion is definitely reached that successive impacts play an unimportant rôle in cumulative ionization.

Photo-impact Ionization.—A similar test of this theory shows that it is consistent with the experiments, and indicates that τ/ρ^2 is about 0.08 for helium. τ is the time interval between excitation of an atom and its emission of resonance radiation, and ρ is the reciprocal of the absorption coefficient for this radiation in the gas at 1 mm. pressure.

PRINCETON UNIVERSITY.

14. THE SCATTERING OF ELECTRONS BY ALUMINUM.

BY C. DAVISSON AND C. H. KUNSMAN.

A PRELIMINARY note on "The Scattering of Electrons by Nickel" was published by the writers in Science for Nov. 25, 1921. Similar observations have now been made on the scattering of electrons by aluminum. For bom-

barding potentials up to 200 volts the maximum intensity of scattering is back along the path of the primary beam; there is no lateral maximum as in the case of nickel, and the distribution is well represented by the relation

$$I_\Psi = k\left[\frac{2\beta - 1}{(2\beta - 1)^2(1 + \cos\Psi) + (1 - \cos\Psi)}\right]^2.$$

These results were expected since the aluminum atom is characterized by only a single strong shell of electrons. Above 200 volts the distribution appears to be the sum of two simple distributions. The added distribution is thought to comprise electrons scattered by atoms of oxygen on the surface of the target. In the compound Al_2O_3 each oxygen atom has a net charge $-2e$ which may be expected to prevent electrons of speeds less than 150 or 200 volts from entering them. It follows that no strong back scattering due to oxygen should occur until this voltage has been passed.

Analysis of the distribution curves below 200 volts indicates that the L-electrons in the aluminum atom are at a distance of about 3×10^{-9} cm. from the nucleus.

Research Laboratories of the
American Telephone and Telegraph Company,
and the Western Electric Company, Inc.,
January 30, 1922.

15. The Ratio of the Two Elementary Charges.

By F. W. Loomis.

Since the oil drops in Millikan's experiments were exactly neutral $\pm$ a small integral number of elementary charges, to 1/1000 of an electron, and since they contained as many as 4×10^{14} protons and nearly the same number of electrons, it follows that the magnitudes of the charges on protons and electrons are equal to one part in 4×10^{17}.

New York University.

16. Ionization and Radiation Potentials and the Size of the Atom.

By Bergen Davis.

A note recently published by Prof. A. S. Eve (Nature, June 30, 1921), points out a possible relation between the ionization potential and the size of the atom.

For some time I had been accumulating data for a similar comparison but from a somewhat different point of view. Eve considers that the outer electron ring is the boundary of the atom. I here assume that the limit of the atom extends beyond this to the point to which an electron must be lifted to produce radiation. If a is the radius of this electron ring and b is the distance from the atomic center that an electron must be lifted to produce radiation, then

$$R = \frac{A}{a} - \frac{A}{b}$$

and

$$I - R = \frac{A}{b}$$

where A is a constant.

The product $(I - R) \times b$ or, for comparison with atomic volumes, $(I - R)\sqrt[3]{\text{A.V.}}$ should be a constant. This product is found to be nearly a constant for elements of the first group. Quite constant for those of the second group. Fairly constant for the inert gas group. The other groups do not show so good constancy. On the whole the product $(I - R)\sqrt[3]{\text{A.V.}}$ is more nearly constant than the product $I\sqrt[3]{\text{at.V.}}$ as proposed by Eve. Paper will be published in detail later.

PHŒNIX PHYSICAL LABORATORY,
COLUMBIA UNIVERSITY.

17. ON THE SPECTRA OF X-RAYS OF SHORT WAVE-LENGTHS.

BY WILLIAM DUANE AND K. C. MAZUMDER.

THIS paper contains an account of experiments on the spectra of x-rays of short wave-lengths, which are now being used extensively in the treatment of malignant and other diseases that lie some distance below the skin.

The x-ray plant, including the spectrometer, has been described in previous papers.

Curves were shown illustrating the distributions of energy in spectra of x-rays produced by constant and alternating voltages of about 165,000 volts. Other conditions being the same, the constant voltage gives a much more intense beam of x-rays than the alternating voltage does. It produces, also, a better distribution of energy in the spectrum, *i.e.*, a greater proportion in the short wave-lengths.

Experiments with various absorbing substances (filters) interposed between the x-ray tube and the spectrometer indicate that copper filters give a much better spectrum than aluminium, and somewhat better than filters composed of compounds of a chemical element of mean atomic weight (such as lanthanum) with one of low atomic weight (such as chlorine) do.

The following table contains the mass coefficients of absorption, μ/ρ, for x-rays of different, short wave-lengths.

Wave-Length, λ.	Mass Coefficient of Absorption, μ/ρ.	
	Copper.	Aluminium.
.1653	1.015	.218
.1477	.745	.194
.1381	.631	.189
.1290	.538	.182
.1124	.399	.167
.0951	.299	.161

The values of the coefficients given by Richtmyer[1] for the wave-length .135 agree with the data in the above table to within a few per cent.

In a paper presented to the Physical Society in 1914 it was shown by one of us that over a wide range of wave-lengths (extending down to .4) the coefficients of absorption for aluminium could be quite well represented by the equation $\mu/\rho = 14.9\lambda^3$. According to Hull and Rice[2] an equation of the form

$$\mu/\rho = k\lambda^3 + s \tag{1}$$

approximately represents the coefficients between the wave-lengths .392 and .147. If we plat our values of the coefficients against the cubes of the wave-lengths the curves representing them are not quite straight lines. They bend downward slightly in the region of short wave-lengths. Our data, however, may be approximately represented by equation (1), if we put $k = 193$ and $s = .13$ for copper, and $k = 15.5$ and $s = .147$ for aluminium. According to the usual interpretation (which may turn out to be somewhat artificial) s represents the mass scattering coefficient.

The thickness of aluminium that absorbs the same fraction of x-radiation as a given thickness of copper depends upon the wave-length. For the wave-length .44 the ratio of the two thicknesses is about 31, whereas for wave-length .095 it is only 6. This fact has enabled us to devise a simple method of estimating quickly the average, or "effective" wave-length of a beam of rays that is not homogeneous. The method consists in measuring by means of an ionization chamber, a photographic plate or a phosphorescent screen the relative thicknesses of aluminium and copper that absorb the same amount of the energy in the beam. A curve gives the corresponding wave-length. The relation between the ratio of the two thicknesses and the wave-length may be obtained from equation (1) by taking the ratio of the two linear coefficients of absorption and putting in the proper values of the constants, k and s. The densities of the copper and aluminium used were 8.92 and 2.7 respectively.

Harvard University.

18. The Crystal Structure of Silver-Palladium and Silver-Gold Alloys.

By L. W. McKeehan.

It is well known that palladium alloys with silver in all proportions forming a continuous series of solid solutions, that crystals of each of these metals possess face-centered cubic space lattices, and that the edge of the unit cube in palladium is about four per cent. less than that in silver. It is also well known that gold alloys with silver in all proportions forming a continuous series of solid solutions, that crystals of gold possess a face-centered cubic space lattice, and that the edge of the unit cube in gold is not more than one per cent. greater than that in silver.

[1] Physical Review, (2), XVIII, p. 13.

[2] Physical Review, (2), VIII, p. 326.

An x-ray analysis of two graded series of alloys extending from pure silver to pure palladium, and from pure silver to pure gold shows that the edge of the unit cube in silver decreases progressively with the addition of palladium, but remains practically unchanged by the addition of gold. The effects of cold-work and of annealing have been observed. Accurate values for the edges of the unit cubes, and the corresponding densities of the pure metals and alloys have been obtained.

RESEARCH LABORATORIES OF THE
AMERICAN TELEPHONE AND TELEGRAPH CO.,
AND THE WESTERN ELECTRIC COMPANY, INC.,
January 31, 1922.

19. PRECISION MEASUREMENT OF CRYSTALS.

BY WHEELER P. DAVEY.

BY simultaneously recording the x-ray diffraction pattern of NaCl on one half of a film, and the pattern of some other crystal on the other half of the same film, it is possible to determine the dimensions of the second crystal in terms of the dimensions assumed for NaCl. On any one film the results so obtained are consistent among themselves. This may be shown by plotting the results on "probability paper." Values of crystal dimensions obtained from different films at different times agree to within one tenth of one per cent.

By this method the side of the body centered cube of CsBr is found to be 4.287 Å. The side of the simple cube (NaCl structure) of RbI is 3.654 Å.

RESEARCH LABORATORY,
GENERAL ELECTRIC COMPANY,
SCHENECTADY, NEW YORK.

20. A SPECTROGRAPHIC STUDY OF ULTRAVIOLET FLUORESCENCE EXCITED BY X-RAYS.

BY J. O. PERRINE.

IN the phenomenon of fluorescence, the emitted radiation has a greater wave-length than the exciting radiation. Therefore, with x-rays as the incident radiation it is not unlikely that fluorescence in the ultraviolet region would result. With this idea as a working basis, a large number of substances were subjected to x-rays and with the aid of an ultraviolet spectrograph, the photographic plate recorded whatever ultraviolet fluorescence there might be.

Fourteen samples of the double salts of uranium, twenty-three oxides and fifty-four samples of miscellaneous salts gave negative results. Exposures varying from one half hour to fifteen hours were made with a Coolidge tube operating at 2 milliamperes, 50,000 volts.

The chlorides of potassium, lithium, rubidium, sodium and caesium gave positive results. Sodium chloride has a very strong band at a wave-length 2,470 Å. Caesium chloride gave the best results with a strong band extending from 5,720 to 2,340 Å. with three points of maximum intensity.

Several samples of willemite were examined, some of which gave positive results. Calcium tungstate, three x-ray intensifying screens and one fluoroscopic screen were examined with varying results.

Quantitative measurements were made of the blackening on the photographic plate by means of a photo-electric cell photometer. Curves showing the distribution of blackening throughout the fluorescent band were plotted, thereby locating the points of maximum intensity.

American Telephone and Telegraph Company.

21. The Grating Space of Mica and the Intensities of the Spectral Orders.

By Bergen Davis and H. M. Terrill.

The grating space of this specimen of mica was measured by an ionization spectrometer in the usual manner. Determinations were made over a number of orders, in one instance to the seventh order.

At the same time measurements were made of the relative intensities of the α_1 and β_1 lines in the various orders. K characteristic of molybdenum.

The grating space was found to be 9.845 Å. for determinations at the first order, increasing to 9.958 at the seventh order. This increase was progressive. This change of grating space with order has been observed by Stenström, who attributes the effect to a small refraction of the x-rays in the crystal. This is not, however, the only explanation. It may readily be shown that a very small curvature of the crystal will produce this effect. The direction of the progressive change in the grating space with order will depend in this case on whether the crystal is slightly convex or concave.

The intensities of the spectral orders showed that the odd spectra were more intense than the even orders, as observed by de Broglie.

The intensities of the α_1 line in the several orders was as follows: (1) 364, (2) 221, (3) 544, (4) 175, (5) 508, (6) 28, (7) 101.

The average intensity of the α_1 line was about 3.5 times that of the β_1 line.

This paper will be published in detail later.

Phœnix Physical Laboratory,
Columbia University.

22. A New Type of Bumstead Electrometer and Accessory Apparatus.

By Harry Clark.

The gold-leaf of this electrometer is not adjustable. The charged plates are 60° sectors of cylindrical tubes, and they are so placed that the concave surfaces face the leaf and the lower edges are close together underneath the leaf. Each of the plates may be moved vertically by means of a micrometer screw. The instrument can therefore be adjusted quickly to any degree of sensitivity while the leaf is kept on any desired part of the scale. When the highest sensitivity is not required, the settings may be duplicated by means

of the screw readings. The shape and position of the plates and the limits of their adjustment are such that accidental contact of the leaf with the plates is impossible. The electrometer has been combined with standard condensers, earth and voltage connections, and a device for attaching various ionization chambers. It has been mounted adjustably on a movable base so that it can be put easily to a great variety of uses.

THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH,
NEW YORK CITY.

23. DYNAMIC CHARACTERISTICS OF HELIUM ARCS.

BY FABIAN M. KANNENSTINE.

HELIUM arcs were formed by impressing a 60-cycle alternating e.m.f. between a Wehnelt cathode and nickel plate in a pyrex tube containing pure helium.

The relation between the e.m.f. impressed and the current through the arc was obtained by Braun tube oscillograms. The arc struck at about 21 volts and the current through the arc increased as the impressed e.m.f. increased in much the same manner as found by K. T. Compton, E. G. Lilly and P. S. Olmstead.[1] However as the voltage decreased quite different results were obtained from those obtained by the above-mentioned authors.

The decreasing part of the curve was above the increasing part and formed a loop, while the arc, instead of breaking at 20 volts, broke at or near zero volts. The decreasing curve instead of being smooth had two sudden changes in curvature, one at or near zero and the other considerably higher but below the striking potential.

These curves seem to indicate that in the arc products are formed which have a very low ionization potential, and a short but measurable life period.

UNIVERSITY OF CHICAGO.

24. THE JOULE EFFECT IN STEEL RODS AT DIFFERENT DRAWING TEMPERATURES.

BY S. R. WILLIAMS AND O. KOPPIUS.

IN this paper a study has been made of the Joule effect in a group of five steel rods at different drawing temperatures. These rods had the following chemical analysis:

Rod No.	Carbon.	Manganese	P.	S.	Si.
1.....	1.34	0.37	0.010	0.018	0.13
3.....	1.27	.27	....	....	....
4.....	1.23	.32	....	....	....
5.....	1.35	.34	....	....	....
6.....	1.27	.37	....	....	....

[1] PHYSICAL REVIEW, (2), XVI, p. 282.

It was interesting to find that beginning with one rod quenched in oil at 788° C. and not annealed there was no initial lengthening as is common to steel, but only as the rods were subjected to higher and higher annealing temperatures did this initial elongation occur. This is important not only for the metallographer but has a great deal of significance for the theory of the process of magnetization in steel rods.

Oberlin College.

25. Effects Obtained with an Alternating Current Sent through a Capillary Electrometer.

By R. D. Kleeman and D. T. Simmonds.

A capillary electrometer was used consisting of a more or less horizontal capillary tube in which mercury and a saturated solution of mercurous sulphate containing one volume of sulphuric acid to seven of water were in contact, the thread of mercury ending in a reservoir of mercury making contact with one of the electrodes, and the thread of solution ending in a reservoir of solution having mercury at the bottom which made contact with the other electrode. An alternating current sent through the electrometer gave rise to a motion of the mercury-solution interface in the same direction as that obtained with a direct current from solution to mercury. Both increase the interfacial surface tension, and thus decrease the electrical double layer, the positive side of which faces the mercury. The alternating current is partly rectified, but the direct current component is in a direction that would tend to make the interface move in the opposite direction. It arises from the fact that the alternating current density across one of the mercury surfaces is much less than that across the other, which gives rise to the corresponding electrical layers being decreased to different extents, giving rise to a difference of potential between them. This shows that a part at least, if not the whole, of the e.m.f. between a metal and a solution is located in the liquid transition layer, as proposed by a theory published in a previous paper.

On putting a condenser in the circuit to cut out the direct current and measuring the pressure necessary to apply to the mercury to keep the interface in position, it was found that the pressure increased approximately linearly up to 10 cms. of mercury which corresponded to about 1.2 volts, above which no change in pressure with change of voltage was obtained. A maximum pressure of 23 cms. of mercury was obtained with a direct current, which also corresponded to 1.2 volts.

Union College,
Schenectady, N. Y.

26. Note on the Formation of Negative Ions in a Gas.

By R. D. Kleeman.

Measurements of the velocity of negative ions in a gas subjected to an electric field usually give larger values at low pressures than inversely propor-

tional to the pressure. This effect, which has been investigated by a number of physicists, is intimately connected with the nature of the formation of ions from free electrons. Loeb has carried out a careful set of experiments (PHYSICAL REVIEW, Vol. XVII., 1921, pp. 89–115) to distinguish between the theory that each liberated electron forms a permanent ion after a certain period (Thomson's theory), and the theory that some of the electrons never get into a suitable state to form ions, while the rest form permanent ions (Wellisch's theory). The experimental results were interpreted to support the former theory. The object of this paper is to point out that Loeb's results, and in general the effect under various conditions, can be as well explained by the theory of ion formation and existence proposed by the writer (Proc. Camb. Phil. Soc., Vol. XVI., pt. 4, pp. 285–298 (1911), and Vol. XVII., pt. 3, pp. 263–279 (1913). According to this theory the electron continually goes through cycles of ion formation and dissociation, during which it is periodically in the free state. This theory, besides, explains a number of other effects.

UNION COLLEGE.

27. NOTE ON X-RAY SPECTRA.

BY WILLIAM DUANE AND R. A. PATTERSON.

L Absorption Limits.—The following table contains new and more accurate measurements of the L_2 and L_3 absorption limits for Au, Pt, and Bi.

TABLE I.

Critical Absorption. L Series of X-Rays.

Grating Space for Calcite, $2d = (6.056 \pm .004) \times 10^{-8}$ cm.

Chemical Element.	L_2.		L_3.	
	$\lambda \times 10^8$ cm.	v/v_∞.	$\lambda \times 10^8$ cm.	v/v_∞.
Pt.....	.9318 ± 3	0.9779	.8918 ± 9	1.022
Au.....	.9008 ± 4	1.0116	.8610 ± 9	1.058
Bi.....	.7871 ± 4	1.1578	.7562 ± 9	1.205

The bearing of these new data on the relations between absorption and emission frequencies is discussed. It is shown that these new values lend support to the x-ray spectra systems proposed by Smekal and Coster.

The relation that an L absorption frequency minus an M absorption frequency should equal an L emission frequency has been shown by us to be approximately true for those cases not eliminated by a "selection principle." With his new and accurate measurements Coster has shown that there is a systematic deviation from the above relation. He ascribes this deviation to the fact that our values for the L absorption frequencies are too small because we have measured the centers of the "drops" in ionization currents due to absorption limits. He and other investigators have found "white lines"

near the absorption limits on their photographic plates and he suggests that the center of this white line constitutes the true position of the absorption limit. We have not yet found any indication of this white line on our ionization current graphs.

The K Series Spectrum of Molybdenum.—Table II. contains our values for the emission and absorption wave-lengths in the K series of Mo. Overn's recent measurements of the emission lines are also given.

TABLE II.

K Series of Molybdenum.

Grating Space for Calcite, $2d = 6.056 \times 10^{-8}$ cm.

Line.	Overn.	Duane-Patterson.	Δ.	Ratio of Intensities.
α_2.....	.7129	.71213 ± 8	.0008	
α_1.....	.7085	.70783 ± 7	.0007	$\frac{\alpha_1}{\alpha_2} = 1.93$ 2d order
β'.....	....	.6320 ± 2	....	$\frac{\beta}{\gamma} = 6.3$ 1st order
β.....	.6322	.63114 ± 7	.0011	
γ.....	.6212	.6198 ± 2	.0014	$\frac{\beta}{\gamma} = 5.5$ 2d order
K.....	....	.6184 ∓ 2	....	

They have been corrected slightly to correspond to the calcite grating space. In the fourth column are given the differences between Overn's values and ours. Overn measured all his lines relative to a reference line at $\lambda = 0.7956$ which value is independent of any x-ray measurements. The values of Δ indicate that our measurements deviate more from Overn's the farther we go away from his reference line.

In the last column of Table II. are the relative intensities of α_1 and α_2, and also of β and γ. The value 1.93 for the ratio of α_1 to α_2 is in close accord with Bohr's predicted ratio of 2.0.

HARVARD UNIVERSITY.

28. ELECTRIC FIELDS DUE TO THE MOTION OF CONSTANT ELECTROMAGNETIC SYSTEMS.

BY S. J. BARNETT.

A SYSTEM B has velocity v relative to fixed axes C. E, E', H, H', ψ, ψ', A, A' are the electromotive and magnetic intensities, and the electric and vector potentials, observed in C and B, at a point fixed in C. $E = -\partial A/\partial t - \nabla\psi$, $E' = -\partial A'/\partial t - \nabla\psi' - [vH']$. Assuming a principle of relativity $E = E'$, $H = H'$, Maxwell proved that the motion produces in C an electric potential $\psi - \psi' = (Av)$. For a constant system, unelectrified in B, $\partial A'/\partial t = 0 = \nabla\psi'$, and $\partial A/\partial t = -(v\nabla)A$; so that $E = (v\nabla)A - \nabla(Av) = E' = [Hv]$. This paper derives from A and v the electric fields for a number of cases. Examples follow. I. Two parallel wires with currents $\pm I$, v being parallel to I.

Here $\partial A/\partial t = 0$ and $E = -\nabla(Av)$. The motion produces charges $\pm q = \pm Iv$ per unit length along the wires. II. Two plane parallel sheets with currents $\pm I$ per unit length, v being parallel to the streamlines. Between the sheets the electric field is uniform and normal to v, the charges per unit area being $\pm q = \pm Iv$. Again $E = -\nabla(Av)$. In both I. and II. the electric moment produced is the vector product of v and the magnetic moment. III. An infinite uniform circular cylindrical current sheet, with magnetic moment M per unit length, and v normal to the axis. (Av) is such as to produce a uniform field with intensity $1/2[Hv]$ within the cylinder, and without the cylinder the field of an axial electric line doublet with moment $[vM]$. $(v\nabla)A$ doubles the intensity inside and cancels it outside. IV. A spherical current sheet with magnetic moment M and current I per unit length of the diameter, v being normal to the magnetic axis. Inside (Av) gives a uniform intensity $-\nabla(Av) = 1/2[Hv]$; outside, the field of a central electric point doublet with moment $[vM]$. $(v\nabla)A$ alters the intensity to $[Hv]$ everywhere. V. Two cylindrical coaxial magnetic poles with a radial field between them, v being parallel to the axis. Here $(Av) = 0$, there are no charges, and $E = (v\nabla)A = [Hv]$. If any system is charged in B, ψ' must be added to (Av). Conductors added to B, and uncharged in B, do not alter $\psi - \psi'$.

THE CARNEGIE INSTITUTION OF WASHINGTON.

MINUTES OF THE MEETING AT STANFORD UNIVERSITY, MARCH 4, 192.2

THE 114th regular meeting of the American Physical Society was held in the lecture room of the Department of Physics, Stanford University, at 1:30, March 4, 1922. Professor Fernando Sanford presided. About 30 members and friends were in attendance. Dinner was served in Stanford Union at 6 o'clock.

The following program was presented:

1. A Note on the Estimation of Tenths. PAUL KIRKPATRICK.

2. The Penetration of Cathode Rays in Molybdenum and its Effect on X-Ray Spectra. D. L. WEBSTER.

3. A Device for Timing Ionization Currents Accurately. D. L. WEBSTER.

4. The Absorption Spectrum of Chloroform in the Near Infra-Red. J. W. ELLIS.

5. On the History of Caloric. FLORIAN CAJORI.

6. A Lunar Diurnal Variation of Earth Potential and Earth Currents. FERNANDO SANFORD.

7. On the Displacement of the North Magnetic Pole of the Earth from the North Geographic Pole. FERNANDO SANFORD.

8. New Spectra of Oxygen and Nitrogen in the Extreme Ultraviolet. J. J. HOPFIELD.

9. A Modification of van der Waal's Equation. W. P. BOYNTON and ARTHUR BRAMLEY. (Read by title).

10. Relativity and the Ether. S. R. COOK.

11. Examples of Motions which have a Terminal Speed. W. J. RAYMOND. Read by title).

12. Restriction of the Electron Beam from a Hot Cathode Braun Tube. L. T. Jones and H. G. Tasker.

13. A Constant Resistance Universal Shunt. H. G. Tasker.

14. The Standardization of Permanent Magnets. Richard Hamer.

15. The Effect of Temperature Changes on Rubber Colloids. Richard Hamer.

E. P. Lewis,
Local Secretary for the Pacific Coast.

1. A Note on the Estimation of Tenths.

By Paul Kirkpatrick.

It was supposed that systematic errors of a particular kind might occur in the process of estimating tenths of the interval between two parallel lines. This supposition was tested by several hundred attempted settings within such an interval one centimeter in width on an instrument made for the purpose.

The results with fifty-nine observers, each making nine different settings, was as follows:

The absolute accuracy of settings, irrespective of the signs of the errors, was highest at the five-millimeter position and lowest at seven millimeters and three millimeters.

The settings of the average observer are given herewith:

Attempted settings	.100	.200	.300	.400	.500	.600	.700	.800	.900
Actual settings	.110	.203	.322	.420	.502	.583	.677	.795	.893

It is seen that the average observer tended always to draw away from the nearer scale ruling. It may be shown in consequence that with observers of this class on the scale here used the probability that a random setting should be ascribed to the wrong millimeter is about .12.

Department of Physics,
University of California.

2. The Penetration of Cathode Rays in Molybdenum, and its Effect on the X-Ray Spectrum.

By David L. Webster.

The penetration of cathode rays in molybdenum was investigated by studying the emission spectrum around the K absorption limit. The stronger absorption on the short-wave side of this limit reduces the emission intensity by about 8 per cent. at 25 kv. and about 16 per cent. at 70 kv., when the cathode rays go in at about 45° to the surface and the x-rays emerge at the same angle. As no rays of this wave-length are produced by electrons of less than 20 kv. energy, the 8 per cent. at 25 kv. may be due largely to surface irregularities, which must be of the order of a micron. The increase at higher voltages measures the average depth of penetration of the cathode rays, which runs up to about 2 microns or so at 70 kv. This is less than one tenth of the depth

one would predict from Whiddington's work on aluminum and gold; but that work was concerned only with the fastest components of a beam after emerging from a metal leaf, so at least a part of this difference must be due to the difference between the average depth and that of the rays that go straightest.

STANFORD UNIVERSITY, CALIF.,
March 4, 1922.

3. A DEVICE FOR TIMING IONIZATION CURRENTS ACCURATELY.

BY DAVID L. WEBSTER.

THE purpose of this paper is to call attention to the possibility of eliminating the human element in the timing of ionization currents in an x-ray spectrometer, by a simple device made from 3 electric bells and a clock escapement. One bell magnet drives the clock escapement with current from a good pendulum clock. The ratchet wheel driven by this escapement carries 2 pins, each of which makes contact with a brush, for one current impulse only. This contact is made at the release of the escapement magnet. and is therefore ready when the next clock current impulse arrives. This next clock current impulse goes from the pin to a magnet that works a lead shutter in the path of the x-ray beam. Thus the accurate timing is done by the master clock, the electric clock merely serving to select the current impulse that will be used.

STANFORD UNIVERSITY, CALIF.,
March 4, 1922.

4. THE ABSORPTION SPECTRUM OF CHLOROFORM IN THE NEAR INFRA-RED.

BY J. W. ELLIS.

To study the region 1.0 μ to 2.8 μ a spectrograph of the auto-collimation type was constructed with two 30° medium flint glass prisms through which the radiation from a 108-watt tungsten lamp passed twice. A bismuth-silver thermopile and a Leeds-Northrup movable-coil galvanometer were used.

Readings were taken as the radiation passed alternately through an empty glass cell in front of a 0.5 millimeter slit and a similar cell filled with chloroform of three millimeters thickness. Correction was made for internal reflection.

In this region lines at 1.011 μ, 1.066 μ, and 1.165 μ were found by Abney and Festing, and absorption maxima at 1.916 μ and 2.652 μ by Iklé.

In the present work five distinct bands were observed with maxima at 1.140 μ (10 per cent.); 1.385 μ (16 per cent.); 1.660 μ (56 per cent.); 1.835 μ (35 per cent.); 2.425 μ (88 per cent.). Per cent. absorption is given in brackets.

These values should be correct to within 100 Å. The calibration curve was drawn through points representing 10 metallic emission lines and 9 infrared solar absorption bands, determined mainly by Paschen with a grating. The average deviation of these points from the smooth curve is less than 50 Å.

The chloroform was manufactured by Squibb's Manufacturing Company and was rated as exceptionally pure.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF CALIFORNIA.

5. On the History of Caloric.

By Florian Cajori.

1. Lucretius must be placed in the list of those who taught the existence of a ponderable heat-substance.

2. Caloric is not an eighteenth-century offspring of phlogiston (as has been claimed); the word "caloric" was coined about 1789, but caloric substances (assumed by some to be ponderable, by others imponderable) are older than phlogiston; no clear views existed on the interrelation of phlogiston and caloric.

3. In America, Hugh Williamson of Philadelphia in 1770 explained heat as due to "rapid vibrations of minute particles"; Benjamin Franklin in 1788 suggested that the subtle fluid, whose vibration is called light, strikes common matter and causes heat; Robert Hare of Philadelphia in 1822 and Denison Olmsted of Yale in 1826 held the materialistic theory of heat; in B. Silliman's books, heat is an "imponderable agent" in 1830, but due to "vibratory movements of molecules" in 1859.

University of California.

6. A Lunar Diurnal Variation in Earth Potential and in Earth Currents.

By Fernando Sanford.

A previous report of observations on a lunar variation of earth potential at Palo Alto was published in Physical Review of October, 1921. The observations there described have been continued. The mean daily range of variation in electrostatic potential of the earth for ninety lunar days in the months of September, October, November and December, 1921, has been, after the solar variation was eliminated, five millimeters on the photographic record, which is equivalent to introducing 1/10 volt between the earth and the electrometer. The effect of the varying distance of the moon from the earth is plainly appreciable. For the four months cited the lunar variation at perigee is 1.4 times as great as at apogee.

By arranging the data on the diurnal variation of the N-S earth-current at Tortosa, Spain, according to lunar days, the influence of the moon on this current is shown. The mean lunar variation in potential difference between the grounded extremities of the line was 18.5 millivolts/kilometer for 27 days in October, 1920. The data used are from Vol. XI., of the Bulletin of *Observatorio del Ebro.*

7. On the Displacement of the North Magnetic Pole of the Earth from the North Geographic Pole.

By Fernando Sanford.

If the primary magnetic field of the earth is due to the rotation of its negative charge, its magnetic axis should approximately coincide with its geographical

axis. It is characteristic of the earth-currents which have been observed that the electrons move around the earth in the direction of the sun's apparent motion. The effect of this induced current around the earth is to weaken the primary magnetic field.

Since the water of the sea is a better conductor of electricity than are the solid materials of the earth, these induced currents will take a water route in preference to a land route. The most nearly continuous east and west water route around the earth will pass about 15 degrees north of the Equator on the American side and about an equal distance south of the Equator on the Asiatic side. Currents flowing from west to east around this route will induce a magnetic field opposite in character to the primary field and with its northerly pole on the Asiatic side of the geographical pole. The resultant northerly pole will accordingly be displaced toward the American side of the geographical pole.

8. New Spectra of Oxygen and Nitrogen in the Extreme Ultraviolet.

By J. J. Hopfield.

The spectrum of oxygen was extended from the former value, λ 990, to the new value, λ 508. Some of the short wave-lengths obtained are approximately (accurate values will be published later) 508, 539, 554, 582, 601, 610, 611, 618, 626, 646, 675, 688, 705, 706, 721, 766, 767, 778, 792, 799, 835, 837. and then 150 lines between 837, and 1,335 Å. This spectrum was obtained with a disruptive discharge at low pressure, the oxygen being pumped through the receiver and connected discharge tube during the exposure. Some of the lines listed above check those obtained by Millikan.

By using a discharge tube of the internal capillary type, but of 2.25 K.W. capacity, with electrodes and capillary oil cooled, the spectrum of nitrogen was extended from 1,400 to 825, and lines at 307 and 362 were also photographed.

The spectrum of air was obtained with the same tube at a pressure of 3 mm. with two minutes exposure to 1,050 Å. These facts,—that by using a powerful discharge the time of exposure can be shortened from one or two hours to as many minutes, and that air does not have prohibitive absorption,—suggest the practicability of building a vacuum grating spectrograph containing a long focus grating. Such a spectrograph, despite its limitations, would be of great usefulness.

Department of Physics,
University of California.

9. A Modification of van der Waals' Equation.

By W. P. Boynton and Arthur Bramley.

The equation for an ideal gas and van der Waals' equation are excellent first and second approximations. A third approximation is suggested:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT\,\frac{T^2/\psi^2}{1 + T^2/\psi^2},$$

which fits Andrews' data on carbon dioxide at least as well as does the equation of Clausius. The correction factor gives a graph resembling the rational curve for specific heats of solids given by Compton.[1]

[1] Physical Review (2), VI, p. 377.

A study of the thermodynamic necessities for a specific heat *not* assumed to have a constant value leads to formulae for specific heat at constant volume, internal energy and entropy respectively:

$$C_v = 2R\frac{3T^2/\psi^2 - T^2/\psi^2}{(1 + T^2/\psi^2)^3} ln\left(\frac{v}{b} - 1\right) + f(T),$$

$$U = 2RT\frac{T^2/2}{(1 + T^2/\psi^2)^2} ln\left(\frac{v}{b} - 1\right) - \frac{a}{v} + \frac{a}{b} + \int_0^T f(T)dT,$$

$$S = R\frac{3T^2/\psi^2 + T^2/\psi^2}{(1 + T^2/\psi^2)^2} ln\left(\frac{v}{b} - 1\right) + \int_0^T \frac{f(T)}{T} dT.$$

We have for the final terms of our solutions

$$f(T) = M\frac{k^2T^2}{1 + k^2T^2},$$

$$\int_0^T f(T)dT = M\left(T - \frac{1}{k}\tan^{-1} kT\right),$$

$$\int_0^T \frac{f(T)}{T} dT = \frac{M}{2} ln(1 + k^2T^2).$$

This assemblage of equations closely approximates van der Waals' equation and the formulæ derived from it on the assumption of constant specific heat through the region of large volumes and high temperatures, gives the same relations for critical volume and pressure, and a somewhat more complicated one for critical temperature, but at low temperatures the specific heat and entropy approach zero values, as the latest studies show they should, so that the value of the entropy here given has no infinite constant of integration, but is finite for all finite values of temperature and volume.

University of Oregon,
Eugene, Oregon,
February 20, 1922.

10. Relativity and the Ether.

By S. R. Cook.

Various hypotheses of relativity are briefly discussed; and it is pointed out that if the ether drift experiment of Michelson, Morley and Miller, should be repeated it would be necessary to take into consideration not only the motions of the observer due to the motion of the earth in its orbit, and the motion of the sun in space, but also the probable motion of our galaxy in space.

Various theories of the ether are also discussed, and it is maintained that our

knowledge of the nature of the ether is such, that at present, any definite theory of relativity based upon the known properties of the ether or the velocity of light is premature.

COLLEGE OF THE PACIFIC.

11. EXAMPLES OF MOTIONS WHICH HAVE A TERMINAL SPEED.

BY WILLIAM J. RAYMOND.

THREE rectilinear motions are selected, involving constant driving force and either an increasing resistance or an increasing amount of effective inertia, real or fictitious. Speeds are (1) $v = c(1 - e^{-kt})$; (2) $v = c \tanh (kt)$; (3) $v = ct(k^2 + t^2)^{-1/2}$. The terminal speed is c. A model has been designed, a massive wheel driven by a descending weight, the speed of the latter retarded: (*a*) by an electromagnetic brake, giving resistance proportional to the speed; (*b*) by a mechanical brake, giving resistance proportional to the square of the speed; (*c*) by increasing moment of inertia of the wheel, caused by radially moving weights; (*d*) by wrapping the driving cord around a screw-threaded shaft, the radius of the shaft decreasing as the speed of the descending weight increases. Method (*a*) illustrates by analogy the growth of electric current in a coil of constant inductance when connected to a battery. In all three types of motion, partition of the activity of the driving weight between change of kinetic energy and "heat-loss," or changes in internal configuration are shown by the model. As far as experiments have been made, there is satisfactory agreement between measurements and the results of mathematical analysis.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF CALIFORNIA.

12. RESTRICTION OF THE ELECTRON BEAM FROM THE HOT CATHODE BRAUN TUBE.

BY L. T. JONES AND H. G. TASKER.

THE usual method is to direct an unrestricted beam from the incandescent cathode against the anode, a small hole in the anode determining the size of the beam. In the present method the anode is an annular ring. A disc with a central hole of about 1 mm. is placed immediately in front of the hot filament, the plane of the disc perpendicular to the axis of the tube. A few volts between this disc and the filament carries the electrons through the hole in the disc, the larger voltage between disc and anode carrying the beam down the tube. The proper adjustment of voltages and dimensions assures a narrow beam down the axis of the tube.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF CALIFORNIA.

13. A Constant Resistance Universal Shunt.

By H. G. Tasker.

The Ayrton-Mather[1] universal shunt for galvanometers provides a multiplying factor n which is independent of the galvanometer resistance, but the effective resistance of the circuit varies widely with n. The new circuit eliminates this variation, while retaining the advantages of the former circuit.

The usual Ayrton shunt is connected to a similar circuit through resistances b_1, b_2, etc., corresponding to values of n. A resistance r_3 occupies a circuit position corresponding to that of the galvanometer. If r be the total resistance shunting the galvanometer and r_2 the corresponding resistance in the added circuit, any values may be chosen for r, r_2, n and the galvanometer resistance R consistent with the ranges desired, whereupon

$$b = r_2 + \frac{r}{n^2} - \frac{r}{n} - \frac{r_2}{n},$$

$$r_3 = \frac{r^2}{R^2} + \frac{r^2}{r^2} - r_2.$$

Department of Physics,
University of California.

14. The Standardization of Permanent Magnets.

By Richard Hamer.

For an investigation on the "ageing of so-called permanent magnets" used in wattmeters, signal devices and electrical meters, it was necessary to devise an expeditious method which would yield results accurate to a hundredth of one per cent. instead of the usual several per cent. The writer succeeded by adopting a null method. The total magnetic flux of a so-called permanent magnet was cut by a falling coil. The current generated was opposed by that from a coil simultaneously cutting the flux of a solenoid carrying an accurately adjusted current. Thus the difference in flux only caused the resultant current through the fluxmeter, and by calibrating the fluxmeter scale an exact balance was not necessary. Due precautions against thermal and magnetic interferences had to be taken. Serious trouble arose because the magnetic distributions for magnets and solenoid are not the same, causing instantaneously unbalanced currents. To reduce the displacement of the fluxmeter coil two methods were proposed, either relating the coil movements so that the peaks of temporary currents coincided, or the use of a cam controlling the relative coil velocities so that both time curves of the temporary currents were of the same type. By accelerating the motion, the first was found sufficient even when the suspension was changed to silver to increase the sensitivity.

University of California.

[1] W. E. Ayrton & T. Mather, Electrician, Vol. 32; 1893-4; P. 627.

15. The Effect of Temperature Changes on the Viscosity of Rubber Colloids.

By Richard Hamer.

This work was undertaken at the University of Toronto for the Scientific and Industrial Research Council of Ottawa. The varieties of rubber were: Kassai, Cancho, Fine Para, Smoked Sheet, Pale Crepe, and Esmeralda, with viscosities ranging from one to three times that of Benzol. The viscosity relative to Benzol was measured at 30° C. before and after temperature changes which consisted of cooling to 6° C., in freezing solid at 0° C., or at − 190° C. by liquid air, or in heating up to 60° C. Cooling the colloidal solutions seemed to cause a slight increase. Freezing solid caused a greater increase. Heating seemed to bring about a slight increase. These results depended apparently on the variety and the concentration. Successive applications appeared to have a cumulative effect, indicating, however, a limiting value. There was a slow recovery with time to the original or an even lower value. This is evidently a sort of hysteresis effect and is remarkably similar to that secured on stretching a piece of vulcanized rubber. It is suggested that temperature changes, particularly freezing solid, cause a temporary polymerization of the rubber molecules. The molecular aggregate is, however, unstable and the forces in solution result in a later depolymerizing action which lasts until equilibrium is reached again.

University of California.

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THE

PHYSICAL REVIEW.

THE FREQUENCY-SENSITIVITY OF NORMAL EARS.

By H. Fletcher and R. L. Wegel.

Synopsis

Minimum Audible Pressure Variation for Tones of 60 to 4,000 Cycles.—The rather discordant results obtained by other investigators are briefly reviewed and are summarized in Fig. 1. In the present research an attempt was made to get results with a definite dynamical significance. A special air-damped telephone receiver held tightly to the ear, was excited by an alternating current of variable frequency from a vacuum tube oscillator provided with special low pass filters to eliminate upper harmonics, and the current strength was changed logarithmically by means of a special attenuator until the threshold was reached. The observations were made in a special *sound proof room* whose construction is described. The probable error is about 25 per cent. To reduce the results to absolute units, the system was calibrated in two ways, both involving the substitution of a condenser transmitter for the ear, the source of sound being a telephone receiver in one case and in the other a small thermal receiver inserted in the ear meatus or in a similar cavity in front of the condenser transmitter. *Mechanical analogues of the vibrating systems involved* in these measurements are described in an Appendix to help make the dynamics clear. While the unknown mechanical constants of the inner ear introduce some uncertainty, the agreement of the two calibrations indicates that the error is not large. *Frequency-sensitivity curves* were obtained for approximately *100 normal and 20 abnormal ears.* So-called normal ears were found to vary widely in relative frequency sensitivity and in absolute sensitivity, and some audiograms show interesting individual peculiarities. But on the average, the minimum audible pressure variation increases regularly from about 0.15 dyne/cm.^{2} at 60 cycles to 0.001 dyne/cm.^{2} at 1,000 cycles and is then approximately constant up to at least 4,000 cycles.

Variation of Sensitivity with Deafness.—People who require throughout the speech range (600 to 4,000 cycles) about 0.1 dyne/cm.^{2} are called slightly deaf; those requiring 1 dyne/cm.^{2} can still follow ordinary conversation; those requiring 10 dynes/cm.^{2} need ear trumpets or other amplifying devices, and those requiring 1,000 dynes/cm.^{2} are totally deaf.

Attenuator for Varying the Current from an Oscillating Tube through Wide Ranges was constructed. It consists essentially of an artificial transmission line with resistance sections of series and shunt arms, so designed as to eliminate interfering effects between the various elements. The range of variation obtained is three million fold.

A LARGE amount of work has been done during the last fifty years in an endeavor to determine in absolute terms the minimum amount of sound that the human ear can perceive. The results obtained

by different investigators have varied throughout a very wide range. Two causes contributed to this: namely, that adequate apparatus was not available, and it was not appreciated that so-called normal ears vary so widely in their ability to hear.

It is important for the proper engineering of the telephone plant to know in absolute terms the sensitiveness of the ears of the average telephone user. For this reason this investigation was undertaken.

In 1870 Toepler and Boltzmann[1] made a determination of earsensitivity. The amplitude of vibration of the air particles in an organ pipe was determined by light interference methods. From the distance to the source at which sound was just audible it was possible to determine the amplitude of vibration of the tone at the threshold of audibility. The results of their measurements together with those to be described below are given in Fig. 1.

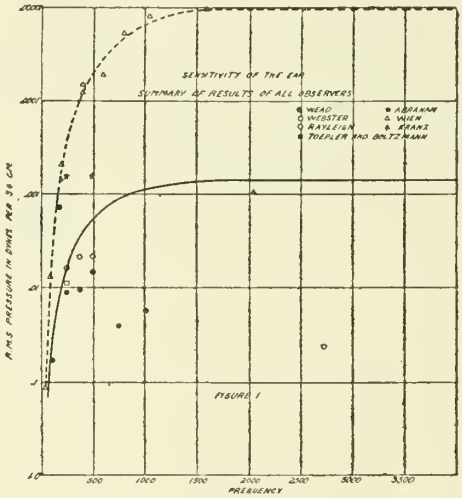

Fig. 1.

It will be noticed that the root mean square value of the pressure is plotted on logarithmic paper. This is necessary because of the wide range of pressures involved. The scale is arranged so that points high up on the plot indicate high ear sensitivity. The ordinates for all of the audiograms—sensitivity frequency curve for the ear—which are to be given later, are drawn on this same scale.

In 1877 Lord Rayleigh[2] used a whistle as a source of sound and calculated the energy emitted by it, from the pressure used in blowing it. He also used a tuning fork mounted on a resonator. From the difference in

[1] Ann. der Phys., Vol. 141, p. 321, 1870.

[2] Proceedings of Royal Society, Vol. 26, p. 248, 1877.

the decay constants of the fork suspended freely in the air and mounted on the resonant box, it was possible to calculate approximately the energy emitted by the box. He made a third measurement using a telephone receiver as a source. The deflection of the diaphragm for direct current was considered the same as for an alternating current when the period was far below the natural period. The former was measured microscopically and consequently when the volume of air enclosed in the ear is known it is possible to calculate approximately the change in pressure on the ear drum from the current flowing in the receiver.

In 1883 Wead[1] used a vibrating tuning fork in an open field as a source of sound. The amplitudes of vibration were made large enough to be directly measured. From the decay constants and the time elapsed before the tone disappeared the absolute values given on the sketch were determined.

In 1889 Wien[2] used a telephone receiver as a source of sound, making measurements of the amplitude of vibration for loud sounds. By assuming that the amplitude increases proportionally with the current it is possible to calculate the amplitude of vibration of the diaphragm at the threshold of audibility. He observed results through a range of frequencies from 50 to 16,000 cycles. The dotted curve in Fig. 1 shows his results.

In 1904 Webster[3] used for his source a so-called "Phone," an instrument so constructed that the emission of sound energy can be calculated. He obtained the value of the ear at 250 cycles of 9.0×10^{-3} dynes per square centimeter.

In 1905 Abraham[4] used as a source of sound a telephone receiver attached to a brass cylinder, the diaphragm forming its base and an earpiece its top. The change in pressure in the cylinder for a direct current in the receiver was determined by a sensitive manometer. He obtained approximately the same sensitivity for the two frequencies 250 and 500 cycles. These frequencies were well below the natural period so that the same proportionality factor was used for obtaining the pressure change as was obtained by the direct current measurement.

In 1921 Kranz[5] used a thermal receiver as a source of sound. From the theory of the thermal receiver and the volume of air enclosed in the ear he calculated the ear sensitivity at 2,048 cycles per second to be 9.6×10^{-4} dynes per square centimeter.

[1] American Journal of Science, 131, Vol. 26, p. 177, 1883.

[2] Ann. der Phys., Vol. 36, p. 834, 1889.

[3] Festschr., F. L. Boltzmann, Leipsig, 1904, p. 1866.

[4] Comptes Rendus, Vol. 144, p. 1099, 1907.

[5] Phys. Rev., (2) XVII, p. 384, 1921.

The results of these various observers are collected together and shown in Fig. 1. It is seen that there is a very wide range between the results of the different observers. For comparison the results which were obtained by us are shown by the heavy line.

The development of the vacuum tube amplifier and oscillator, condenser transmitter and thermal receiver has given us precision apparatus which has made it possible to make accurate measurements of ear sensitivity. In this investigation for most of the measurements the source of sound was an air-damped telephone receiver. This was held tightly against the ear and by means of a special vacuum tube oscillator alternating current at different frequencies supplied to it. The current was then reduced by means of a specially constructed current attenuator until the tone in the receiver was just audible.

All of the measurements were made in a room which was especially constructed to eliminate all outside noises. The top, the bottom, and the sides of this room were built of a number of alternate layers of loose felt and sheet iron, the final inside layer being felt covered with cloth. It is extremely important that all noise interference be eliminated in making measurements near the threshold of audibility. In a room having the ordinary noises from the street the threshold point may be shifted to ten times its value in a quiet place, and in very noisy places this may be increased to 1,000 times.

The construction of the attenuator played an important rôle in making it possible to determine accurately the threshold of audibility. It consists essentially of an artificial transmission line having resistance sections of series and shunt arms. It is so designed mechanically that the terminals of the receiver can be placed across this line and moved along it at will. This is accomplished by simply moving a single dial switch, the complete scale of which represents a variation in current of more than three million fold. The network is so designed that each step corresponds to a certain fractional decrease in potential across the receiver terminals. As the contacts are moved uniformly from the input end toward the output end of the network the intensity of sound coming from the receiver decreases logarithmically. Considerable difficulty was encountered in the construction of this attenuator owing to the high attenuations involved. It was only after considerable experimenting and adjusting that it was possible to eliminate interfering effects due to the capacity between the various elements and to the small resistance in the heavy lead wires. A schematic circuit drawing and a photograph of the complete attenuator is given in Fig. 2.

The air-damped telephone receiver was constructed so that the dia-

phragm was damped by a small film of air in a manner similar to that used in the capacity transmitter as described by Crandall and Wente.

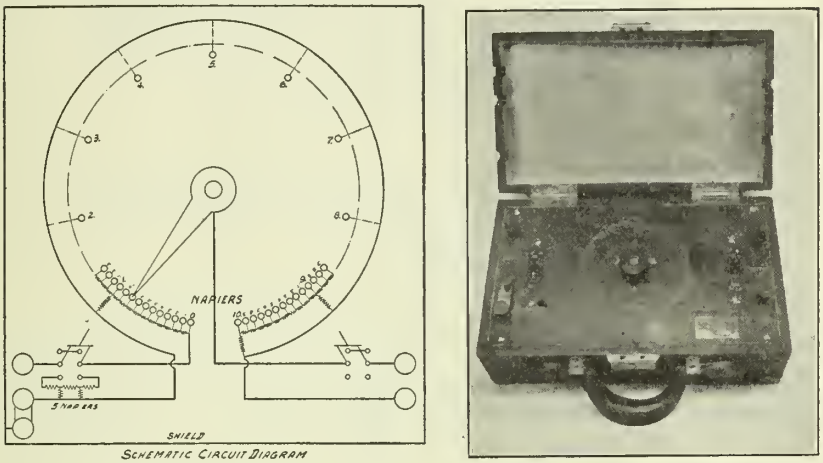

Fig. 2.

The vacuum tube oscillator was equipped with special low pass filters. These were designed so that all harmonics produced in the oscillator were reduced in amplitude more than one thousand times before they entered the attenuator. It is important that such precautions be taken especially at the low frequencies for it will be seen from the results which were obtained that a tone at 1,000 cycles per second requires only 1/60th as much pressure variation for audition as for a tone at 100 cycles per second. Two methods of calibrating this system were used, both depending upon the calibration of the condenser transmitter. The method of calibrating the latter has been described by Crandall[1] and Wente.[2] It consists essentially in determining the voltage generated with a measured pressure change in the diaphragm. The calibration obtained by means of an enclosed thermal unit was checked at low frequencies by an alternating pressure produced by a positively driven piston and at 600 and 1,000 cycles it was further checked by calculation[3] from the motional impedance of a permanent magnet receiver which was clamped tightly over the condenser transmitter.

The first method of calibration was made possible by the construction of a high-quality telephone system described in a paper given at the Washington meeting of the Physical Society, April 23, 1920. A schematic dia-

[1] Crandall, Phys. Rev.. (2) XI, p. 449 (1918).
[2] Wente, Phys. Rev., (2) X, p. 39. 1917.
[3] R. L. Wegel, Journal A. I. E. E., Oct., 1921.

gram of this circuit is given in Fig. 3. By adjusting the potentiometer it

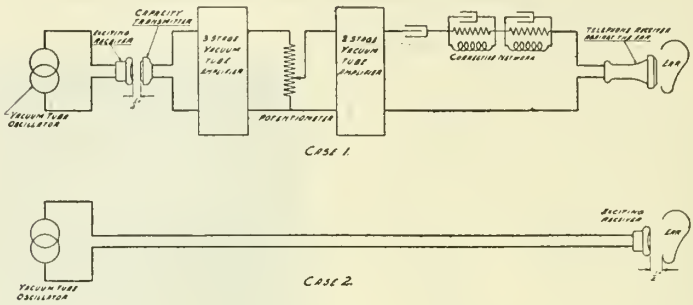

Fig. 3.

was possible to make the tone coming from the system receiver *B* (Case I.) sound exactly as loud as that produced when the ear was held in the same position as the condenser transmitter (Case II.). This reading of the attenuator was found for all frequencies from 100 to 2,000 cycles. Since the sound energy striking the condenser transmitter was known in terms of the voltage generated by it, the energy going from the receiver of the system into the ear of the observer could then be calculated from the potential difference at the terminals of the condenser transmitter and the reading of the attenuator.

To make a measurement a potential difference of known magnitude and frequency was applied at the terminals of the condenser transmitter and sufficient attenuation was introduced into the system to make the sound from the receiver inaudible. The attenuation was then gradually removed until the sound just became audible. From the amount of attenuation for this condition and the voltage impressed upon the terminals of the condenser transmitter the pressure variation in the ear was calculated. Four or five readings were taken in this way which gave an average value having a probable error of 20 or 30 per cent. in the determination of the pressure variation. This method was used for making tests with 11 different observers—seven men and four women, through a range of frequencies from 130 to 2,000 cycles per second. The average of the results is shown by curve 1 in Fig. 4.

In the second method of calibration a thermal receiver unit small enough to be inserted in the external auditory meatus of the ear and completely close it, was used. It consisted of a series of short Wollaston wires enclosed in a small brass capsule with small holes communicating with the outside air. A small chamber was made in front of the calibrated condenser transmitter diaphragm equal in volume to that of the external ear. The thermal receiver was inserted in a hole in this chamber

in such a way as to make it airtight. A sketch showing the details of the coupling between the condenser transmitter and thermal receiver is shown at the bottom of Fig. 5.

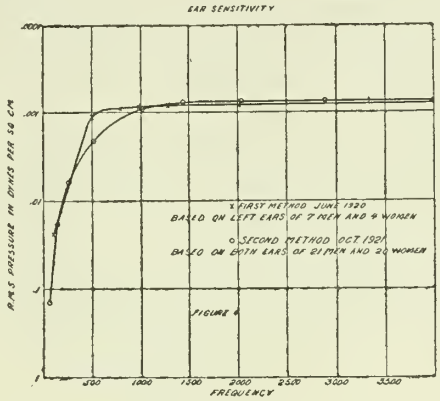

Fig. 4.

The relation between the voltage impressed upon the thermal receiver and the pressure exerted by it on the condenser transmitter diaphragm was then determined experimentally. The apparatus used in this work is illustrated in Fig. 5.

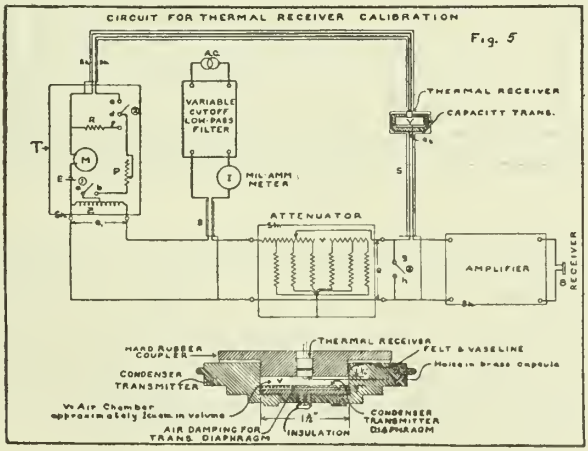

Fig. 5.

By means of this arrangement a known electromotive force is introduced into the condenser transmitter circuit which is equal to that generated by the condenser transmitter when actuated by the thermal receiver. This equality is established by listening at the receiver *B*. By means of the switches the tone from this receiver is first produced by the

condenser transmitter and then by current through the attenuator. When the latter is adjusted so that the tone sounds equally loud from either source it is evident that the equality is established. In this way a calibration curve was made showing the pressure variation produced by the thermal receiver unit against the condenser transmitter at various frequencies when a unit e.m.f. is impressed upon the thermal receiver circuit contained in the box T.

The first thermal receiver unit which was used had a single aperture in the brass capsule of approximately .1 millimeter in diameter. The calibration curve for this receiver is shown as curve a in figure 6. An addi-

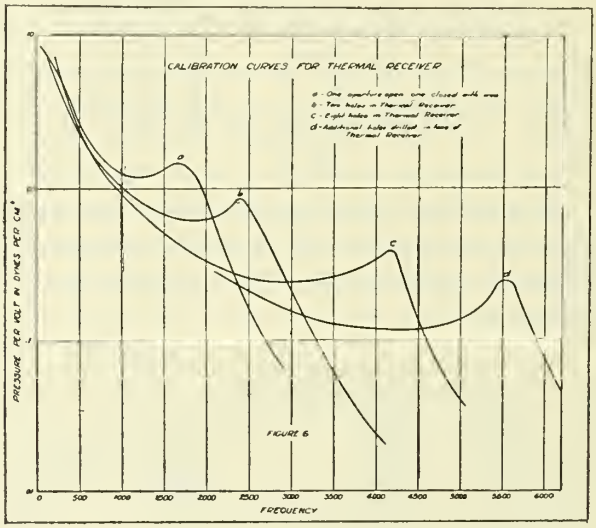

Fig. 6.

tional hole was drilled in the receiver and then it was recalibrated, the curve b showing the result. Similarly, by drilling more holes in the receiver the calibration curves c and d were obtained. The shifting of the resonant peak in this manner is explained by Rayleigh's formula which gives the resonant frequency of an enclosed sphere of air having a small opening. According to this formula

$$f = \frac{a}{2\pi}\sqrt{\frac{C}{V}}$$

where f is the resonant frequency in cycles per second; a the velocity of sound in air; C the diameter of the connecting circular aperture and V the volume of the resonator. In this experiment the volume of the enclosed air was approximately 1 cubic centimeter. By applying the for-

mula and using this figure and .1 centimeter for the circular aperture the resonant frequencies for *A* and *B* calculate to be 1,710 and 2,400 respectively, which agrees with the observed result. Curves *c* and *d* were finally used for calibrating the air-damped receiver system.

Using these two thermal receivers the minimum audible pressure was calculated from the minimum audible current when the thermal receiver was inserted in the ear. Simultaneous measurements were made with five people using first the air-damped receiver and then the thermal receiver. From a comparison of the results the latter system was calibrated. The probable observational error in this determination was found to be 8 per cent. in the range of frequencies from 500 to 3,000 cycles.

It is seen from the manner in which the measurements were made that the first method of calibration gives directly the pressure variation at the opening of the external ear provided only that the ear reflects the sound waves the same as does the condenser transmitter when placed in the same position. Also in the second method the pressure variation which is computed is that which would be exerted upon the ear drum provided that it had the same stiffness as the condenser transmitter diaphragm. Since the ear drum moves and its mechanical impedance at some frequencies may be comparable with that of the ear chamber the actual pressure variation against the ear drum may be somewhat less than that given in the curves.[1] As a matter of fact the two methods give approximately the same results as is indicated by the two curves 1 and 2 in Fig. 4. This agreement seems to indicate that the pressures which are given are not very greatly different from those which are actually exerted upon the ear drum. As indicated by these curves the average sensitivity for normal ears varies from .15 dyne at 60 cycles to .001 dyne at 1,000 cycles. Between 1,000 and 4,000 cycles per second the sensitivity is approximately constant and equal to .001 dyne per square centimeter.

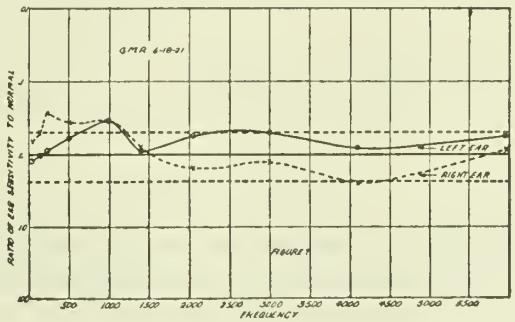

Fig. 7.

[1] For a discussion of the mechanical reactions involved see the Appendix.

Figure 7 shows a typical audiogram for a person of normal hearing. At any given frequency, the average sensitivity for all the observers of normal hearing as shown in Fig. 4, was used as the norm in plotting this and succeeding audiograms. Fig. 8 gives the audiograms of twenty women. A set of curves for twenty-one men were taken which was practically a duplicate of Fig. 8. The probable observational error is

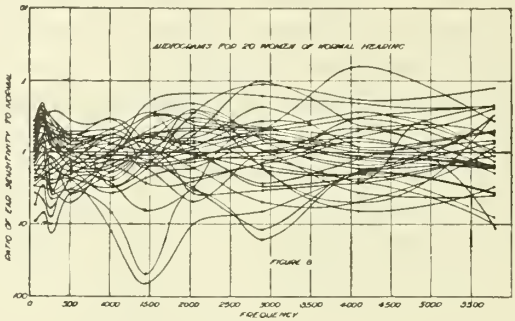

Fig. 8.

approximately 25 per cent. The probable deviation of any observed value from the average normal, including the observational error and the variation in the sensitivity of different normal ears, is approximately in the ratio of one to two.

It will be seen that an audiogram oscillates more or less about normal and that different ears vary greatly in this respect. Fig. 9 is a represen-

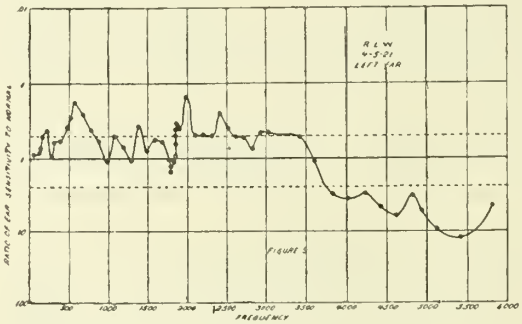

Fig. 9.

tative careful run made on a single ear and shows that a large number of small peaks actually occur. It might be noted that these vary more or less from day to day in a single ear. In averaging the audiograms of a large number of people these small peaks would cancel and consequently it was not necessary to make such careful runs on all the forty-one people who were tested.

Figure 10 shows an audiogram of a person who was supposed to have

Fig. 10.

normal hearing but for some cause his ears acted like a filter cutting off at a frequency at about 3,000 cycles. Audiograms for people of various types of deafness show striking differences in their relative frequency sensitivities. It is expected to make a complete report of work along this line in the very near future. It is sufficient here to give from our general experience the amount of sound volume in the speech range that is required to make people of various degrees of deafness hear. Persons who have normal hearing require approximately 1/1000 dynes per square centimeter in order to hear sounds in this range. Persons who require a pressure variation of 1/10 dynes per square centimeter are called slightly deaf. Those who require one dyne are partially deaf but can usually follow ordinary conversation. Those who require 10 dynes belong to that class who use ear trumpets or deaf sets to amplify the speech waves. A pressure variation of approximately 1,000 dynes can be felt and produces a sensation of pain. For practical purposes it may be assumed that people who experience no auditory sensation at these pressures are totally deaf.

This shows that among people who can follow ordinary conversation there is a range in ear sensitivity of more than 1,000 and among people who are noticeably deaf there is another range of 1,000, making a total range of more than a million for people who can hear or be made to hear by means of amplifying devices.

In conclusion we desire to express our indebtedness to Messrs. F. W. McKown, F. H. Graham and C. E. Dean who have assisted in various phases of this work.

APPENDIX.

From a dynamical standpoint the phrase "sensitivity of the ear" as it is usually used is rather indefinite. When a figure is given in ergs per second, the rate of flow of energy through an area equal to that of the ear opening in an unobstructed wave, is meant. This has no simple relation theoretically, at any rate, to the net rate of flow of energy into the ear when the head is placed as an obstruction to the wave. The distortion of the sound field by the head varies greatly with frequency. Similarly, there is no simple relation between the energy flowing into the ear and that transmitted to and absorbed by the ear drum or by the cochlea. In the experiments recorded above, some attention was paid to the experimental set-up so as to make the figures given have a more definite dynamical significance. Sensitivity is given in terms of the alternating (root mean square) pressure to produce a minimum audible sensation. Just what is meant by pressure is best explained with reference to the schematic diagrams shown in Fig. 11.

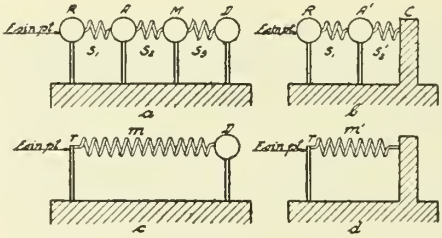

Fig. 11.

Diagram *a* represents schematically the vibratory system involved in the case of the measurements by means of reproduction ratio, simplified, of course, for the sake of easy demonstration. A series of four weights supported by springs and connected by springs is shown. If each of these elements be considered as being made up of properly distributed combinations of dynamical coefficients of mass, stiffness and friction (*i.e.*, so as to give a proper action and reaction between R and D), we may regard the element R as representing the telephone receiver diaphragm acted on by a force $F \sin pt$ of the electromagnet; A as air space between the receiver diaphragm and the opening to the ear; M as the external ear canal and D the ear drum with its attached apparatus. The second diagram, *b*, represents schematically the set-up for calibration, in this case, of the telephone receiver R with the capacity transmitter C. In this case A' represents the air space between the receiver and the capacity transmitter C which may be regarded as practically rigid. The calibration consists of measuring the pressure on C per unit of force

$(F/\sqrt{2})$ acting on the receiver diaphragm. If we assume that the sound fields between receiver and head and between receiver and capacity transmitter are identical, then the elements s_2 and A are identical with s_2' and A' respectively. The area of opening of the external ear canal is not equal to the area represented by the capacity transmitter diaphragm so s_2 and s_2' are not identical, but if it is agreed that allowance can be made for the difference by using pressure per square centimeter, the relation between s_2 and s_2' may be assumed to be known. The calibration then gives the force in dynes per square centimeter acting on M if M is held rigid. This corresponds to having the auditory canal stopped. Since, however, M, the air in the ear canal, is movable, the force on this area is different from that given by an amount depending on the vibratory characteristics of M and D and their relation to A. The curves of sensitivity may then be considered to be (within the error of measurement and of experimentally matching a and b) the pressure sensitivity of the entire auditory apparatus including the vibratory characteristics of the air space between the receiver and head, the ear canal and the drum.

The dynamical system involved in the measurement with the thermal receiver is less complex. Diagram c represents the system in this case. The mechanical impedence of the thermal receiver is practically of pure elasticity represented by the vertical spring r. This represents the elasticity of the active cushion of air around the thermal element which includes a volume of approximately .01 cc. (see paper by H. D. Arnold and I. B. Crandall in Physical Review, July, 1917, on the thermal receiver), and assumes the measurements to be made well below the resonance of the air cavity as shown in Fig. 6. The volume enclosed in the ear is about 1 cc. so that the elasticity m representing this element is negligibly small. D represents the ear drum. Diagram d is the schematic representation of the calibrating system in which r is the thermal receiver, m', a cavity in which the receiver was inserted in front of the capacity transmitter C. m' was made equal in volume to the volume of the ear cavity m. Since the reaction in both systems c and d on r are negligibly small, because of the lack of stiffness of the spring (air chambers m and m'), this measurement gives the overall sensitivity of the ear including the vibratory characteristics of the drum and 1 cc. of air enclosed in the external auditory canal.

The close check between curves obtained by both methods (see Fig. 4) indicates that the difference between the two vibratory systems is very small within the range of frequencies measured.

Research Laboratories of the
American Telephone and Telegraph Company
and the Western Electric Company, Inc.,
November, 1921.

ON THE CHARACTERISTICS OF HIGHLY SENSITIVE DISCHARGE POINTS.

By John Zeleny.

Synopsis.

Discharge from Sensitive Points as a Function of Applied Voltage.—The points were prepared by grinding sewing needles to a fine point and then holding them an instant in an alcohol flame. The discharge always starts *impulsively* and the voltage at which this occurs, if *gradually* increasing potentials are applied, may differ greatly on successive trials, but is never below a value B for a given point. A current once started persists when the voltage is lowered below B but breaks suddenly at a definite potential C. If a voltage above B is *suddenly* applied to a point a current will eventually start after a time interval which on the average is the shorter the higher the voltage applied.

Voltage Range for Counting Rays.—The entrance of each alpha particle or other "ray" along the axis of a counting chamber containing a sensitive point gives rise to a *momentary* discharge, provided the voltage used is above a limit A and below B. If the voltage is above B a *continuous* current is started. In a case cited A, B and C were respectively 1,730, 1,875 and 1,820 volts.

Explanation.—The sensitiveness of points is determined by a compact layer of gas molecules which offers a large resistance to the passage of ions but which may be penetrated and dissipated by ions with high speeds. The initiation of a discharge is ordinarily dependent upon the fortuitous entrance of a "ray" into a region, near the point, whose extent increases as the voltage used increases.

In a recent article[1] some consideration was given to so-called sensitive points, and evidence was presented which on the whole favors the view that the lag phenomena of these points are due to the presence on their surfaces of a layer of gas molecules which, owing to the condition of the surface, is more uniformly packed and therefore less easily penetrable by ions than is the case for a similar layer on the surfaces of points which do not show lag in the commencement of a discharge.

While most sensitive points are erratic in their behavior it is possible to prepare points which continue steadily for days to show a large retardation in the commencement of the current and which in other respects exhibit a uniform behavior. Such points are used in a certain method[2] of counting the number of alpha or beta particles, or gamma-ray pulses which enter a counting chamber, since under proper conditions these agencies initiate momentary discharges that are readily observed.

A careful study has been made of the characteristics of some of these

[1] J. Zeleny, Phys. Rev., 16, p. 102, 1920.

[2] See A. F. Kovarik, Phys. Rev., 13, p. 272, 1919.

uniformly and highly sensitive points and some features have been observed which are of interest. The points were prepared from sewing needles in the way described by Kovarik (loc. cit.) who grinds the end to an extremely fine point and then places it for an instant into an alcohol flame. The surface of the point after this treatment shows a uniformly glossy appearance under the microscope.

One arrangement of the apparatus which was used in the experiments to be described is shown on the insert (not drawn to scale) in Fig. 1. The sensitive point was enclosed in a brass chamber *I* (about 1.5 cm. in diameter) which had a small opening in the bottom for admitting rays and which was connected to a voltmeter and the source of potential, a static machine arranged to give a steady voltage whose magnitude could easily be changed.

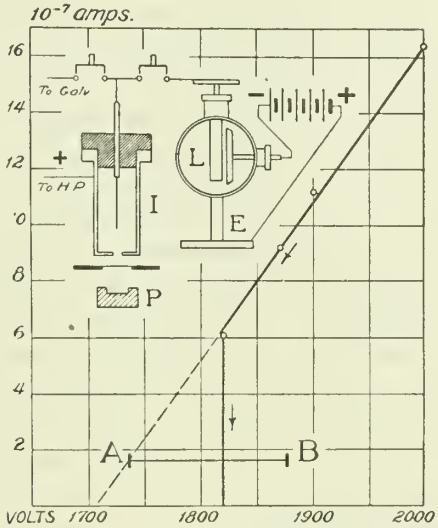

Fig. 1.

The sensitive point was connected either to ground through a galvanometer or to the leaf *L* of an oscillating-leaf electroscope,[1] *E*. The apparatus is shown as used for a negative point discharge.

When the polonium source *P* was in the position shown the alpha rays from it entered the chamber *I* through the opening in the bottom, after passing through a very thin foil of aluminum.

In the absence of the radioactive material, the positive discharge from a certain point, to be used as an example, was found to commence suddenly with a current of 5 to 10 microamperes at minimum voltages ranging from 2,800 to 3,500 volts. An explanation will be given below of

[1] J. Zeleny, Phys. Rev., 32, p. 581, 1911.

this variation in the potential at which a current starts, a variation whose magnitude may be even larger than the values just given. A current once started continued to flow with applied potentials below that required to start it, but at 1,820 volts it suddenly broke from a value of 0.6 microampere to zero.

When, however, alpha particles from the polonium source P were allowed to enter the counting chamber I through the opening shown, then for a certain range of potentials the entrance of each alpha particle gave rise to a momentary current which caused the electroscope leaf to be attracted to and then repelled from the charged plate situated near it. Owing to the short period of motion of the leaf a rapid succession of particles may be counted.

The lowest potential of the chamber for which the entrance of an alpha particle resulted in a momentary current from the sensitive point in question was 1,730 volts, and such momentary currents were caused by entering alpha particles[1] for potentials up to 1,875 volts, but beyond this last potential the entrance of an alpha particle into the chamber started a current which continued indefinitely. The curve in Fig. 1 serves to visualize more clearly the relationship described. The full line curve shows how a current, once started, diminishes with decrease of potential until at 1,820 volts it suddenly breaks and falls to zero. The dotted line is an extrapolation curve showing how the current would have decreased to zero had it not broken. The region of potentials marked by the limits AB is that in which each alpha particle causes a momentary current only. This region begins but a little above the voltage for which an unretarded current should begin to flow and extends well beyond the voltage at which a continuous current stops. For any voltage above B, an alpha particle starts a current whose magnitude is given by the ordinate of the curve in the figure.

If alpha particles are supplied to the ionization chamber in very rapid succession the indicating instrument apparently shows a continuous current even for potentials between the limits A and B since the instrument cannot follow the individual impulses. In a case like this, however, the current stops as soon as the source of radiation is removed, whereas when a continuous current is once started it continues to flow after the removal of the radiation which started it.

A discharge from a point whether sensitive or insensitive is to be looked upon as having its origin in ions produced in its neighborhood by one or more of the radiations from radiaoctive bodies. Sensitive points

[1] It was noticed a number of times that a point did not begin to register alpha-ray "kicks" until some seconds after the alpha particles had commenced to enter the "counting" chamber.

are distinguished from insensitive ones in that with sensitive points, ions coming to the surface layer are, for potentials below B, unable to give their charges to the metal surface instantly on their arrival and a temporary state of polarization is created which momentarily reduces the electric field in the neighborhood of the point below that requisite for ionization by collision and the discharge accordingly stops. Under these circumstances an alpha particle for example produces an impulsive discharge whereas it would have started a continuous current with an insensitive point the surface layer on which does not offer a serious obstacle to the passage of ions.

It must be assumed, since the impulsive discharges from sensitive points may follow one another quite rapidly, that the condenser formed by the ions on the surface layer of a point is a very leaky one.

When the potential used is above the limit B the ions coming to the surface layer have sufficient speed to disrupt this layer and so a continuous current results. On the other hand a current cannot persist if the voltage is diminished to a value for which the ions do not have sufficient speed to prevent the formation of the obstructing surface layer.

We are now in a position to consider why in the absence of special radioactive material the minimum potential required to start a continuous current is found to be such a variable one. Since a single alpha particle will, as has been stated, start a continuous current if the voltage of the chamber is above B, it is evident that even when no outside source of rays is present, the current may be started by an occasional alpha particle projected from the inside walls of the enclosing vessel. Beta rays and gamma-ray pulses may also produce the same effect. Hence when the voltage applied to one of these points, in the absence of extraneous radiations, is gradually but continuously increased, which is the usual method employed for finding the voltage required to start a current, the value of this voltage for which a current starts is dependent upon the fortuitous entrance, into the region surrounding the point, of an alpha or beta particle or a gamma-ray pulse.

If the ionizing agent happens to enter just as the voltage B is reached the current will start with a potential of the lowest value, whereas if the radiation comes unusually late after the voltage B is passed the current will start at a comparatively high potential. Also, the maximum voltage observed will on the average be the higher the more rapidly the potential is raised.

There is another element present however which remains to be explained, for, when voltages above the value B are *suddenly* applied to the

chamber in the absence of a source of rays, the time interval between the application of the voltage and the commencement of the current depends upon the magnitude of the voltage, and above a certain voltage the current appears to start as soon as the voltage is applied. An example will illustrate this behavior. With a certain sensitive point, alpha rays started a permanent current when the potential used was above 1,500 volts, but produced "kicks" only for potentials between 1,400 and 1,500 volts. Observations were made of the time interval between the sudden application of a given voltage and the appearance of a current, when no extraneous radiation was used. The individual time intervals observed for any voltage showed large variations among themselves, nevertheless the average times of about 20 trials for each voltage show a rapid decrease as the voltage was raised, as is seen from the table which follows. In the region between 1,400 and 1,500 volts, where "kicks" only were produced by the various radiations, the average time between "kicks" was about 3 minutes. For higher voltages the average time after the voltage was applied before a current started to flow was

	52	seconds for	1,500	volts
	22	" "	1,550	"
	6	" "	1,600	"
	2	" "	1,650	"
about	1	" "	1,700	"

Obviously the number of "rays" entering the region concerned must on the average have been the same in all of these cases and hence some other factor not yet considered must have had a predominant influence in starting the discharge.

It is seen from Fig. 1 that in the arrangement used for counting "rays," the rays are directed more or less toward the sharp end of the sensitive point and accordingly the ions produced by them are pulled through the strongest part of the field to a very small area on the point. For voltages between A and B these ions and those resulting from them by collision are sufficiently numerous to give a measurable, momentary discharge before the action is stopped by the polarization previously discussed. With a voltage above B the ions have velocities sufficiently large to remove molecules from the surface layer and they are numerous enough to keep the surface clear for the maintenance of a continuous current.

In the absence of special radioactive material, however, the chance rays that enter the chamber may come from any portion of the chamber surface and may move in any direction whatsoever. In general, there-

fore, the ions will not be produced by the rays in the most favorable position for starting a current from a sensitive point and the potential necessary to start a discharge will in each case depend upon just where the initial ions were produced. The higher the voltage the less restricted is the location and direction which a ray must have in order to start a current and accordingly the sooner will a discharge begin after the voltage is applied. It must be remembered also that the number of ions introduced into any region must be greater than a certain minimum number if the multiplication of these ions by the process of collision is not to be interrupted in its initial stages through the laws of chance that govern ionizing collisions.

Sloane Laboratory,
Yale University,
January 27, 1922.

ON REFLECTION FROM A MOVING MIRROR AND THE MICHELSON–MORLEY EXPERIMENT.

By E. H. Kennard and D. E. Richmond.

Synopsis.

Reflection of Plane Waves from a Moving Mirror.—Formulæ for the direction and speed of the reflected wave with reference to the moving system are derived.

Theory of the Michelson-Morley Experiment.—The angle through which a ray is deviated by a moving mirror contains a second-order term in v/c, which it was thought by Righi would account for the negative result of this experiment. In this article, the relative *ray-paths* through the interferometer are traced, the *phase difference* is calculated and the *interference pattern* is obtained, and it is found that the second-order term produces only an imperceptible alteration in the fringe pattern. It is concluded, therefore, in agreement with Villey, that the usual *interpretation* of the experiment in favor of Relativity still holds.

THE experiment of Michelson and Morley is of such fundamental importance in the Special Theory of Relativity that it seems worth while to examine the theory of this experiment from every angle. The accepted interpretation has recently been attacked by Righi[1] and defended, in turn, by Villey.[2] But Villey does not bring out clearly the nature of the secondary phenomenon discovered by Righi and its relation to the main phenomenon, so that an independent investigation of the question seems worth while, and that is the object of the present paper.

We shall follow Righi in limiting the discussion to the case of parallel incident rays and shall assume that all the rays and the direction of motion lie in the plane of the apparatus.

1. Relative Wave Kinematics.

The interference pattern is most easily worked out to the required degree of approximation from the standpoint of the moving apparatus (without the relativity contraction, of course).

To obtain the law of reflection, in Fig. 1 let POP' represent the path in the ether of a ray reflected from a mirror MOM' moving with a velocity v inclined as shown at an angle γ (positive in figure) with its face. Let $v = \rho\, c$ where c = the velocity of light. Let us draw $PR = \rho\ (PO)$ $P'R' = \rho\ (OP')$, both parallel to v: then ROR' is the path of the ray relative to the mirror. Again, on wave-fronts drawn through P and P'

[1] Le Radium, Vol. 11, p. 321, 1919.

[2] Comptes Rendus, Vol. 171, p. 298, 1920.

respectively choose points S and S' so that SM drawn parallel to the motion equals ρ (PO) and $M'S' = \rho\ (OP')$. Then clearly the Huyghens wavelets produced by reflection start out successively from points along SOS', and the angles POS and $P'OS'$ will therefore be equal. Let the relative incident and reflected angles be μ and μ' respectively. Then the trigonometry of the figure leads ultimately to the result, as far as terms in ρ^2,

$$\mu' - \mu = -\rho^2 \sin 2\gamma \sin^2 \mu. \tag{1}$$

This equation expresses the secondary effect of reflection whose influence upon the results was the object of Righi's investigation.

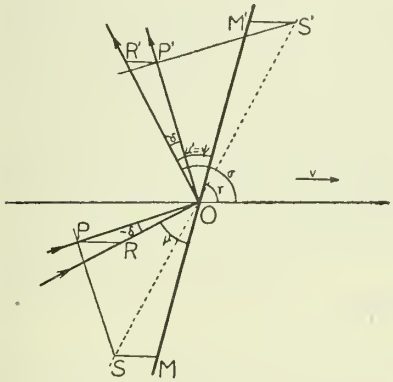

Fig. 1.

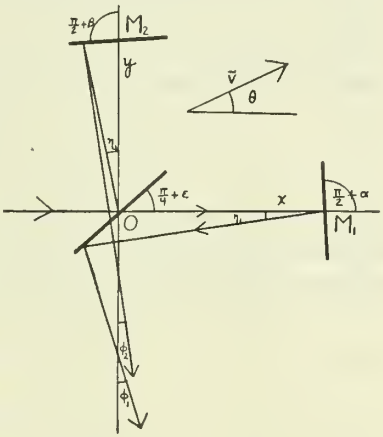

Fig. 2.

Paths of Corresponding Rays.

To calculate phases we shall find it convenient to use the speed V, with which the intersection of a wave with any given line in the moving system moves along the line. Let the angle between the relative ray and the given line be ψ and that between relative ray and direction of motion, σ. Fig. 1 will serve again if we let MOM' represent now the given line and OR', the relative ray. Then a wave traverses simultaneously OM' along the line MOM' and OP' along the ether ray, so that $OM' : OP' :: V : c$; whence we find ultimately, as far as terms in ρ^2,

$$\frac{1}{V} = \frac{1}{c}\left\{\cos\psi + \rho\cos(\psi - \sigma) + \frac{\rho^2}{2}\left[(1 + \cos^2\sigma)\cos\psi + \sin 2\sigma \sin\psi\right]\right\}. \tag{2}$$

Finally, the wave makes with the normal to the relative ray an angle (negative in the figure)

$$\delta = -\rho \sin \sigma. \tag{3}$$

2. Ray-Paths in the Michelson-Morley Experiment.

We shall now trace through the interferometer the two (relative) rays into which an incident ray is divided at the half-silvered plate.

Let us assume that all of the rays are parallel to the plane of the apparatus and let us take axes in this plane (see Fig. 2), the x-axis parallel to the incident light and intersecting the half-silvered plate in O and one mirror in M_1, and the y-axis through O and intersecting the other mirror in M_2. Let the direction of motion be parallel to the same plane and make an angle θ with the x-axis. Let the plate be inclined to the x-axis at an angle $[(\pi/4) + \epsilon]$ and let the normals to the mirrors M_1, M_2 make angles α, β respectively with the negative x- and y-axes. Let $OM_2 = \mathrm{L}$, $OM_1 = L + l$.

Since the effect noted by Righi is of the order ρ^2, we shall reject all terms in higher powers of ρ. Furthermore, we shall suppose α, β, ϵ and l/L all to be small, and, since the formation of the principal set of fringes and the principal effect due to motion both involve the first power of these quantities, we shall simplify the calculation by rejecting all powers of these quantities above the first (except in terms in ρ); and we shall drop these quantities entirely in the coefficients of ρ^2.

Then for the reflection of the transmitted ray OM_1 at $M_1, \gamma = \pi/2 + \alpha - \theta$, $\mu = \pi/2 + \alpha$; hence by (1) $\mu' - \mu = -\rho^2 \sin 2\theta$, approximately, and the ray returns toward O at an angle

$$\eta_1 = 2\alpha - \rho^2 \sin 2\theta \tag{4}$$

with the negative x-axis. Then at the half-silvered plate $\gamma = \pi + \pi/4 + \epsilon - \theta$, $\mu = \pi/4 + \epsilon - \eta_1$, whence approximately $\mu' - \mu = -\rho^2 \cos 2\theta/2$, and the ray proceeds toward the observing telescope at an angle with the negative y-axis

$$\phi_1 = 2\epsilon - 2\alpha + \frac{\rho^2}{2}(2 \sin 2\theta - \cos 2\theta). \tag{5}$$

Similarly, for the reflected ray, at O

$\gamma = \pi/4 + \epsilon - \theta$, $\mu = \pi/4 + \epsilon$, $\mu' - \mu = -\rho^2 \cos 2\theta/2$, and this ray leaves O at an angle

$$\eta_2 = 2\epsilon - \frac{\rho^2}{2} \cos 2\theta$$

with the y-axis; while at the mirror M_2

$\gamma = \pi + \beta - \theta$, $\mu = \pi/2 + \beta - \eta_2$, $\mu' - \mu = \rho^2 \sin 2\theta$, and the ray therefore returns downward at an angle

$$\phi_2 = 2\beta - 2\epsilon + \frac{\rho^2}{2}(2 \sin 2\theta + \cos 2\theta) \tag{7}$$

with the negative y-axis.

Comparing (5) with (7) we note that the secondary effect expressed by (1) results in changing the direction of both of the final rays but not by an equal amount. This inequality leads to an interesting consequence discussed below.

3. Phase Difference of the Waves.

Let us now find the time taken by a wave of each train to return to O.

For the transmitted wave we apply (2) to the motion of its intersection with the x-axis. The journey from O to M_1 takes a time OM_1/V with $\psi = 0, \sigma = -\theta$. The term in ρ contains the distance OM_1 multiplied by $\cos(\psi - \sigma)$: this is simply the projection of OM_1 upon the line of motion and we shall denote it by $(OM_1)_v$. Similarly, for the return journey $\psi = \eta_1$, $\sigma = \pi + \eta_1 - \theta$ and the term in ρ contains the factor $(M_1O)_v = -(OM_1)_v$. Hence this wave returns to O after a time approximately equal to

$$t_1 = \frac{L + l}{c}\left\{2 + \rho^2(1 + \cos^2\theta)\right\}. \tag{8}$$

Similarly, for the reflected wave we follow its intersection with the y-axis to M_2 and back: going, $\psi = \eta_2$, $\sigma = \pi/2 + \eta_2 - \theta$; returning, $\psi = \phi_1$, $\sigma = 3\pi/2 + \phi_1 - \theta$, and this wave returns to O after the approximate time

$$t_2 = \frac{L}{c}\left\{2 + \rho^2(1 + \sin^2\theta)\right\}. \tag{9}$$

Thus the transmitted wave reaches O a time $(t_1 - t_2)$ behind the reflected wave where, to our degree of approximation,

$$t_1 - t_2 = \frac{2l}{c} + \frac{\rho^2 L}{c}\cos 2\theta. \tag{10}$$

4. The Interference Pattern.

The interference pattern is now easily obtained by drawing the simultaneous positions of waves in the two trains. The fringes will evidently have the form of planes perpendicular to the plane of the rays and nearly parallel to the y-axis; as a matter of fact, (2) gives the same speed for both sets along Oy, to our degree of approximation, hence the inclination of the fringe-planes to O lies beyond the range of our formulas.

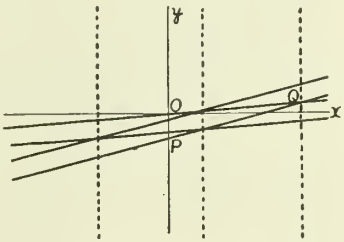

Fig. 3.
Interference pattern.

To locate the central fringe, let OQ, PQ (Fig. 3) be simultaneous positions

of a transmitted wave and of the corresponding reflected one, each inclined to its ray-normal by the angle δ as given by (3): then the central fringe (zero retardation) passes through Q at a distance $x_0 = OQ$, approximately, from the y-axis. Now the reflected wave passed O a length of time $(t_1 - t_2)$ ahead of the other, hence $x_0/V = t_1 - t_2$, where V is the speed of the intersection of the reflected wave along the line OQ, the latter being regarded as fixed in the apparatus. V is thus given by (2) with $\psi = 3\pi/2 + \phi_2 - \phi_1 - \delta_1$, $\sigma = 3\pi/2 + \phi_2 - \theta$, while by (3) $\delta_1 = -\rho \sin(3\pi/2 + \phi_1 - \theta)$; inserting values from (5) and (7) and retaining only the usual terms, we find

$$\frac{1}{V} = \frac{1}{c}\left\{2\alpha + 2\beta - 4\epsilon + \rho^2 \cos 2\theta\right\}. \tag{11}$$

Hence, taking the value of $t_1 - t_2$ from (10), to our degree of approximation

$$x_0 = \frac{2l + \rho^2 L \cos 2\theta}{2\alpha + 2\beta - 4\epsilon + \rho^2 \cos 2\theta}. \tag{12}$$

The same calculation yields the distance between fringes, w, if we substitute w for x_0 and a light-period, λ/c, for $t_1 - t_2$; hence, letting n = number of fringes between O and the central one,

$$w = \frac{\lambda}{2\alpha + 2\beta - 4\epsilon + \rho^2 \cos 2\theta}, \qquad n = \frac{x_0}{w} = \frac{2l + \rho^2 L \cos 2\theta}{\lambda}. \tag{13}$$

5. Discussion.

The quantity actually made the object of observation by Michelson and Morley was the variation of n with θ, and the field was actually viewed in a plane through mirror number 2 instead of in a plane through Ox, but this makes no difference in the results deduced here. If the apparatus is turned from $\theta = 0°$ to $\theta = 90°$, n varies through $\Delta n = 2\rho^2 L/\lambda$ and Δn fringes will appear to pass O: this is the observable effect as predicted by Michelson and Morley.

The effect of the term in ρ^2 in the law of reflection is thus confined to terms of higher order than the principal one. This term is responsible for the terms in ρ^2 in the denominators in (12) and (13), and accordingly leads only to the following effects:

(1) The fringe-width w and the distance to the central fringe x_0 are each increased in the ratio $1 + \rho^2 \cos 2\theta/(2\alpha + 2\beta - 4\epsilon)$, motion parallel to the incident rays expanding the fringe pattern and motion at right angles contracting it. But since ρ^2 might easily be as small as 10^{-8} this change of dimensions is probably beyond the reach of experiment (2).

The fringes will vanish only when $2\alpha + 2\beta - 4\epsilon = -\rho^2 \cos 2\theta$. Thus in the case of perfect alignment ($\alpha = \beta = \epsilon = 0$) and perfect equality of path ($l = 0$) fringes will still be visible for which

$$w = \frac{\lambda}{\rho^2 \cos 2\theta}, \; x_0 = L, \; n = \frac{\rho^2 L \cos 2\theta}{\lambda}. \tag{16}$$

These were the fringes studied by Righi, who appears to have confounded them with those actually observed. As the apparatus is turned through 90° the center of the system remains fixed while the fringes broaden, disappear, and return exactly to their original positions. Thus in the two "principal" positions ($\theta = 0°$, $\theta = 90°$) the field appears exactly the same: this fact is the cornerstone of Righi's argument. Obviously, however, the intensity is not the same at intermediate positions, as was pointed out by Villey, and under the proper conditions fringes might be observed to pass O during the rotation.

These fringes are, however, too broad to be readily observed. For sodium light their width would be something like $6 \times 10^{-5}/10^{-8} = 6{,}000$ cm. Thus in the apparatus used when alignment was perfect the field would appear uniformly illuminated, but the intensity would undergo fluctuations during rotation which might, in principle at least, be detected with a photometer.

It appears certain therefore that the famous negative result of Michelson and Morley was not due to any second-order effect of motion upon reflection at the mirrors.

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February, 1922.

PROBLEMS OF QUANTUM THEORY IN THE LIGHT OF THE THEORY OF PERTURBATIONS.

BY PAUL S. EPSTEIN.

SYNOPSIS.

1. It is shown in the following paper that the physical purport of *Delannay's* method in the theory of perturbations consists in successive approximation of a given motion by means of a set of conditionally periodic motions.

2. It is further shown, that at every degree of approximation two possible cases must be taken into account. In the one the motion of the system is periodic with respect to a certain variable, in the other this variable performs a libration.

3. In both cases formulæ for carrying through the calculations are given, fit for the purposes of the theory of quanta.

4. A modification of *Delaunay's* method, due to *Whittaker* is applicable to one of the two cases only and is therefore incomplete.

5. *Delaunay's* method (in our modification) quite automatically yields at every degree of approximation the special coördinates, looked for in the theory of quanta.

§ 1. INTRODUCTION.

THE method explained in the following pages was worked out by the author several years ago for the purpose of quantizing the helium atom.[1] Its principle, however, turned out not to be new[2] and to have been already the foundation of a procedure applied by Delaunay[3] in the theory of the moon. Though Delaunay did not use the notions of the "conditionally periodic system" and of the "angular variables," the introduction of these concepts changes only the formal side of the line of thought. We shall therefore in the following refer to our procedure as "*Delaunay's method.*"

In the meantime methods of the theory of perturbations were introduced into the theory of quanta by others also: J. M. Burgers[4] adopted a manner of treatment due to Whittaker, while N. Bohr[5] dealt with the problem of finding the coördinates suitable for quantization in slightly disturbed systems. The rules given by Bohr were applied with great

[1] An exposition of the method with application to the problem of three bodies was given by the author in October, 1917, and the two following ones were communicated by him to the Association of Swiss Naturalists in 1919 (Cf. the brief report: Verh. der Schweis. Naturforschenden Ges., 2. Teil, p. 83, 1920).

[2] I am indebted for valuable quotations of literature to some letters of Mr. J. M. Burgers in fall of 1917.

[3] Delaunay, Théorie du mouvement de la lune (Mémoires de l' Académie des Sciences, Vol. 28, 29), Paris, 1860, 1867.

[4] J. M. Burgers, Verslagen Amsterdam, XXXVI., p. 115, 1917.

[5] N. Bohr, Kgl. Danske Vedensk. Selsk., Nat. Afd., 8. Raekke IV. 1, 1918.

success by Kramers[1] for explaining the gradual increase of the Stark effect with the electric field. This work however does not by any means make superfluous the publication of my modification of Delaunay's method. I believe on the contrary, that it can claim some interest for several reasons:

First, this procedure is particularly applicable to the theory of quanta because of the fact that the real motion can be regarded as *successively approximated by conditionally periodic motions*. A way is given for finding a set of conditionally periodical motions which approximate the real motion successively closer and closer. These systems are, however, not of the simplest type studied by Haeckel, and there therefore arises the problem of investigating a more general kind of conditionally period motion (§§ 4, 5). We shall see that all theorems which are valid in Haeckel's [2] case can be extended also to the new type. In particular there still remains the possibility of describing the motion by angular variables (§ 6). The principles of the theory of quanta, as they were laid down by the author[2] for conditionally periodic systems, can therefore be applied unchanged to whatever degree of approximation one desires.

Second, at any step of approximation there may appear two essentially different types of motion which determine the method of passing to the next step. Both Delaunay himself and Poincaré [3] pointed out this alternative, but, as it seems, not with sufficient emphasis; at least, this important discrimination is entirely ignored in Whittaker's modification[4] already referred to. Therefore this modification does not exhaust the problem and is in many cases inapplicable (§ 9). To show this we lay stress on making clear the physical meaning of the transformations used.

Third, the special forms, in which the theory of perturbations is carried through, start from the existence of a small constant parameter, by which the perturbation function may be developed. Such a parameter however is not available in all problems of the theory of quanta. Whittaker's method is free from this restriction, but comprises, as already mentioned, one of the two possible cases only. The center of gravity of our considerations lies therefore in showing how the numerical calculations can be carried through in the second case, not included in Whittaker's theory, without using a constant parameter (§§ 7, 8).

In so far as these three points are concerned, our investigation lies

[1] H. A. Kramers, ibidem, 8. Raekke, III. 3, 1919.

[2] P. S. Epstein, Ann. d. Phys., *50*, p. 815; *51*, p. 168, 1916.

[3] H. Poincaré, Les méthodes nouvelles de la mécanique celeste, Vol. II, §§ 200 and ff. Paris, 1893.

[4] E. T. Whittaker, Proc. London Math. Soc., *34*, p. 206, 1902; Analytical Dynamics, p. 404, Cambridge, 1917.

in the region of general dynamics and will be only partly new to the astronomer.

Fourth and last, the method opens interesting aspects of the theory of quanta, dealt with in § 10. It is shown there, that the problem of coördinates suitable for quantization, is solved quite automatically by the method: it is sufficient to go on from approximation to approximation in order to find always the right variables. In the special case when the undisturbed motion is periodic, the coördinates found by our method agree exactly with those resulting from the rules given, for this case, by Bohr. Also for some other cases discussed by Bohr our method gives closely similar results. There exists, however, a difference, for Bohr regards the possibility of exact quantization as an exception, and generally expects, for a disturbed motion, indeterminate values of energy; whereas from the point of view of our theory, exact quantization is the normal case, and indeterminate values of energy are at least much rarer than Bohr implies. The decision between the two points of view seems to lie within experimental possibilities.

§ 2. From the Transformation Theory of Dynamics.

We proceed to put together several theorems, to be used in this and in the following communication.

Let the differential equation of a mechanical system of f degrees of freedom be given in the canonical form

$$(1) \qquad \frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i}, \qquad \frac{dq_i}{dt} = \frac{\partial H}{\partial p_i}, \qquad (i = 1, 2, 3, \cdots f),$$

where the *Hamiltonian function* $H(p, q, t)$ depends upon the *momenta* p_i, upon the *coördinates of position* q_i and upon the time t. By the system of equations

$$(2) \qquad \begin{cases} p_i = p_i(P_1, \cdots P_f;\ Q_1, \cdots Q_f;\ t), \\ q_i = q_i(P_1, \cdots P_f;\ Q_1, \cdots Q_f;\ t) \end{cases}$$

one may pass to the new variables P_i, Q_i. It remains to be determined, in which case the coördinates P_i, Q_i are again *canonical* variables.

In the following we shall have to deal with the two special cases, in which the functions (2) are either independent of time, or contain time in the form of a linear term $A_i t$, (resp. $B_i t$), where A_i and B_i are constants. The criterion for P_i, Q_i being canonical coördinates can then be expressed by means of the so-called "Lagrange's parenthesis"

$$(3) \qquad (a, b) = \sum_{i=1}^{f} \left(\frac{\partial p_i}{\partial a} \cdot \frac{\partial q_i}{\partial b} - \frac{\partial q_i}{\partial a} \cdot \frac{\partial p_i}{\partial b} \right)$$

in the following way

$$(4)\qquad \begin{cases}(Q_j, Q_h) = 0, \\ (P_j, P_h) = 0,\end{cases} \qquad (P_i, Q_h) = \begin{cases}0 & \text{for} \quad j \neq h, \\ 1 & \text{"} \quad j = h.\end{cases}$$
$$(h, j = 1, 2, \cdots f).$$

We shall discuss the above two cases separately:

1. A transformation, independent of time

$$(2')\qquad \begin{cases}p_i = p_i(P_1, \cdots P_f;\ Q_1, \cdots Q_f), \\ q_i = q_i(P_1, \cdots P_f;\ Q_1, \cdots Q_f),\end{cases}$$

satisfying conditions (4) is called a "*contact-transformation.*"[1] The most interesting property of these transformations is, that both systems p_i, q_i and P_i, Q_i have the same Hamiltonian function: *the Hamiltonian function is invariant with respect to contact-transformations.* We see further from the form of equations (4) that they are entirely independent of the special form of the Hamiltonian function, so that they can be satisfied by a proper choice of the transformation equations (2′) alone. We can express this important circumstance by the following statement:

Let a system of coördinates p, q be given, canonical with respect to two Hamiltonian functions H and H^*. If we succeed in finding another system of coördinates P, Q, which are canonical with respect to H, they will be canonical with respect to H^* also.

By a well-known theorem of Jacobi's the contact transformation can be defined by one single function of the variables P_i and q_i

$$(5)\qquad W = W(P_1, \cdots P_f;\ q_1, \cdots q_f),$$

from which the transformation-equations can be derived in the form

$$(5')\qquad p_i = \frac{\partial W}{\partial q_i}, \qquad Q_i = \frac{\partial W}{\partial P_i}.$$

2. The case in which equations (2) assume the form

$$(2'')\qquad \begin{cases}p_i = p_i'(P_1, \cdots P_f;\ Q_1, \cdots Q_f) + A_i t, \\ q_i = q_i'(P_1, \cdots P_f;\ Q_1, \cdots Q_f) + B_i t,\end{cases}$$

where A_i and B_i are constants, and conditions (4) are satisfied, we shall name a "*Delaunay-transformation.*" The difference between this and the first case is that here there exists no invariancy of the Hamiltonian function. On the contrary, the new variables, P_i, Q_i, are canonical with respect to a *changed* Hamiltonian function

$$(6)\qquad H^* = H + \sum_{i=1}^{b}(A_i q_i - B_i p_i).$$

[1] E. T. Whittaker, Analytical Dynamics, Chapter XI. Cambridge, 1917.

A glance at conditions (4) shows us that they do not restrict the choice of the constants A_i, B_i. The applications below deal with the case in which the dependence on time only of the coördinates of position q_i is given by the values of the constants B_i $(i = 1, 2, \cdots f)$. It follows from the remark just made that the choice of the quantities A_i is entirely at our discretion. In particular we can put these constants equal to zero, which leads to the following simplest form of the Delaunay-transformation

$$(7) \qquad \begin{cases} p_i = p_i^*(P_1, \cdots P_f;\ Q_1, \cdots Q_f), \\ q_i = q_i^*(P_1, \cdots P_f;\ Q_1, \cdots Q_f) + B_i t, \\ \qquad H^* = H - \sum_{i=1}^{b} B_i p_i. \end{cases}$$

p_i^*, q_i^* are functions which, taken alone (*i.e.*, putting B_i equal to zero) yield a contact-transformation.

§ 3. Delaunay's Method.

Let the motion of a system be given by the Hamiltonian function

$$H(p_1, \cdots p_f;\ q_1, \cdots q_f).$$

For the sake of simplifying our considerations we suppose forces to be conservative, and therefore time to be lacking as an explicit argument of H. But we shall see that these considerations can be enlarged without any essential change for certain forms of explicit dependence on time.

To carry through the integration of this problem, we shall, with Delaunay (l.c.), use the following method of approximation: we choose a conditionally periodic motion, having the Hamiltonian function H_1, in such a way that it is as near as possible to the given motion, and if we split function H in two terms

$$(8) \qquad H = H_1 + R_1,$$

so that the remainder R_1, or the "*perturbation function*," becomes as small as possible. The motion, defined by H_1, is called the "*first intermediate motion*."

One of the important features of conditionally periodic motions is that they can be described by so-called "*angular variables*," *i.e.*, it is possible to introduce by means of a contact-transformation

$$(9) \qquad \begin{cases} W = W(u_1, \cdots u_f;\ q_1, \cdots q_f), \\ p_i = \dfrac{\partial W}{\partial q_i}, \qquad w_i = \dfrac{\partial W}{\partial u_i}. \end{cases}$$

a new set of canonical coördinates (w_i) and momenta (u_i), possessing the following properties:[1]

1. The state of the system (for instance its original coördinates p_i, q_i) is a periodic function of the variables $w_1, w_2, \cdots w_f$, having the period 2π.

2. The variables w_i are linear functions of time

$$w_i = \Omega_i t + \delta_i. \tag{10}$$

The coefficient Ω_i is called the "*average motion*."

3. The momenta u_i are constant and are proportional to Planck's quantum of action h:

$$u_i = \frac{h}{2\pi} n_i, \tag{11}$$

n_i meaning whole numbers, the so-called "*quantum-integers*."

4. Transformation (9) being accomplished, H becomes a function of the momenta u_i only and is independent of the variables w_i.

The theory of conditionally periodic motions (cf. § 6) affords the means of establishing transformation (9) for the intermediate motion defined by function H_1. Using the theorem stated in § 2 we see, however, that the variables introduced by those transformation-equations prove to be canonical with respect to the whole Hamiltonian function H also. Of course they lose their physical meaning: referred to the system determined by H, neither are the quantities w_i linear functions of time, nor are the quantities u_i constant. But since the form of functional dependence is retained, p_i and q_i remain in a formal respect periodic functions of the variables w_i. If within the limits of variation of p_i and q_i the perturbation function is a regular function of these coördinates, as we shall suppose it to be, it will be itself a periodic function of the angular variables, and in most cases it may be expanded into an f-fold Fourier-series. At least the possibility of such an expansion is supposed in all that follows.

On the other hand, the term H_1 of the Hamiltonian function will continue to depend on the quantities u_i only:

$$H = H_1(u_1, \cdots u_f) + \sum_{m_1}, \sum_{m_2} \cdots \sum_{m_f} b_{m_1, m_2, \cdots m_f} \begin{matrix}\cos\\ \sin\end{matrix} (m_1 w_1 + \cdots + m_f w_f), \tag{12}$$

where the coefficients b are functions of the momenta u_i.

Let b be that one of the coefficients which has the largest numerical value. We are to consider the system defined by the Hamiltonian function

$$H_2 = H_1(u_1, \cdots u_f) + b(u_1, \cdots u_f) \begin{matrix}\cos\\ \sin\end{matrix} (m_1 w_1 + \cdots + m_f w_f). \tag{13}$$

[1] Cf. C. G. Charlier, Die Mechanik des Himmels, Vol. I., p. 94, Leipzig, 1902; also P. S. Epstein, Ann. d. Phys., *51*, p. 176, 1916.

We shall prove in §§ 4, 5 that such a function again represents a conditionally periodic system. This we can choose as the *second intermediate motion*, putting similarly to (8)

$$(8') \qquad H = H_2(u, w) + R_2(u, w),$$

and denoting by R_2 the remaining part of the *Fourier*-series. Instead of u, w we have now to introduce the angular variables u', w' of the conditionally periodic motion, given by (13); then H_2 is dependent on the quantities u' only, while R_2 must be rearranged in a new f-fold Fourier-series, proceeding by the arguments w'.

By this transformation the periodic term of the Fourier-series (12) having the largest numerical value is taken away and converted into a part of the aperiodic term. The same procedure applied to the periodic term, second in absolute value, leads to the *third intermediate* conditionally periodic motion, and takes away this term also. Going on successively in such a way, we can make the numerically important terms of the Fourier-series vanish one after another (retaining only their aperiodic parts), and we can proceed to conditionally periodic motions which approximate more and more closely the real motion, until the desired degree of precision is reached.

This procedure is particularly well adapted to the theory of quanta, operating with that particular function which is the most important one for that theory. In most applications, indeed, the problem is to find the expression of energy in terms of the quantum-integers (11), and to express in terms of the momenta u_i the Hamiltonian function of that intermediate motion by which one wishes to close the approximation.

Of course the question remains unsettled as to whether the procedure sketched in this paragraph is a convergent one. We can point out only that Delaunay used it in the theory of the moon, and arrived at a good agreement with observation, and that the theory of quanta does not by far aspire to the degree of precision achieved by Delaunay and his successors. We shall briefly revert to this question again in § 10.

§ 4. Extended Theory of Conditionally Periodic Motions.

We are now to supply the proof that the Hamiltonian function, given by equations (13) § 3 defines in fact a conditionally periodic motion. We confine ourselves to the case of the cosine, because that of the sine results from the first one by a simple shift of phase of the argument. We start from the equation of energy

$$(14) \qquad H_2 = H_1(u_1, \cdots u_f) + b(u_1, \cdots u_f)\cos(m_1w_1 + \cdots + m_fw_f) = \alpha,$$

because the Hamiltonian function, if independent of time, is known to express the energy α of the system.

Our first object is to bring about a separation of variables, and we succeed in this by a simple contact-transformation:

$$(15)\qquad \begin{cases} W = u_1'\cdot(m_1w_1 + \cdots + m_fw_f) + \sum_{i=2}^{f} u_i'w_i, \\ u_i = \dfrac{\partial W}{\partial w_i}, \qquad w_i' = \dfrac{\partial W}{\partial u_i'}, \end{cases}$$

from which,

$$(16)\qquad \begin{cases} u_1 = m_1u_1, \quad u_2 = u_2' + m_2u_1', \quad \cdots \quad u_f = u_f' + m_fu_1', \\ w_1' = m_1w_1 + \cdots + m_fw_f, \quad w_2' = w_2, \quad \cdots \quad w_f = w_f. \end{cases}$$

We introduce the quantities u_i', w_i', instead of u_i, w_i, into our equation (14)

$$(17)\qquad H_2 = H_1'(u_1', \cdots u_f') + b'(u_1', \cdots u_f') \cos w_1' = \alpha.$$

Now only one single coördinate of position appears in the energy equation; the other coördinates do not enter in the Hamiltonian function at all, and are therefore called "*cyclic variables.*" It follows from this that their corresponding momenta are constant (in virtue of the canonical equations $u_i' = -\partial H/\partial w_i'$). *Thus the separation of variables is accomplished:* Equation (17) gives us the relation between the two variables u_1' and w_1', while the quantities α, u_2', $\cdots$ u_f' must be considered as constant.

We will now investigate equation (17) in order to determine if it represents a conditionally periodic motion. Some properties of that type of motion we have already mentioned in § 3. But their characteristic feature is this, that the coördinates, determining the position of the system, are either already of such a nature that the state of the system is *periodic* in them when they grow without limit (in the manner of a plane angle), or that they perform "*librations,*" *i.e.*, swing backwards and forwards between two fixed limits. In the special case in which the Hamiltonian function is quadratic in terms of the momenta, the conditions for the occurrence of such motions and the properties of the same were studied by Haeckel (cf. § 3). In particular Haeckel showed that, separation of variables being possible, one can always choose the constants of the motion in such a way that it assumes the characteristics of conditional periodicity. We shall prove that the conditions in the case of the form of Hamiltonian function given by equation (17) are quite similar. This form is on the one hand more special than Haeckel's, the dependence on the coördinate w_1' being a fixed one, but on the other hand it is more general, leaving entirely open the dependence on the coördinate u_1'.

For the sake of simplifying our notation we shall again drop the accents on the letters. $u_2, u_3, \cdots u_f$ playing only the part of constants, we write for short

$$H = H_1(u_1) + b(u_1)\cdot\cos w_1 = \alpha. \tag{17'}$$

This equation establishes a functional dependence between u_1 and w_1, of which, on account of the physical meaning of the problem and on account of the symbol u_1, referring to a mechanical momentum, we can conclude in advance as follows: (1) u_1 is an analytic, not infinitely many-valued function of $\cos w_1$. (2) It follows from this that we know the whole path of u_1 if this quantity is given between the limits $0 \leq w_1 \leq \pi$, the values of u_1 in the adjacent intervals $-\pi \leq w_1 \leq 0$, $\pi \leq w_1 \leq 2\pi$, etc., resulting from the former ones by reflection. (3) u_1 has, at least in part of the region between 0 and π, real values. We shall suppose it to be real in the vicinity of $w_1 = 0$, a restriction which does not limit the generality of our conclusions.

If in a diagram we plot w_1 as abscissa and u_1 as ordinate, the tangent of the angle at any point of the curve is

$$\frac{du_1}{dw_1} = -\frac{\dfrac{\partial H}{\partial w_1}}{\dfrac{\partial H}{\partial u_1}}.$$

The maxima and minima of the curve are given by the condition

$$\frac{\partial H}{\partial w_1} = -b(u_1)\sin w_1 = 0, \tag{18}$$

the turning points (*i.e.*, the maxima and minima of w_1) by

$$\frac{\partial H}{\partial u_1} = \frac{\partial H_1}{\partial u_1} + \frac{\partial b}{\partial u_1}\cos w_1 = 0. \tag{19}$$

To simplify our argument we shall suppose that b does not vanish in any point of the curve, and that u_1 assumes no infinite values, though our conclusions would be the same if these possibilities were admitted. The maxima and the minima of the curve lie at $\sin w_1 = 0$, *i.e.*, $w_1 = 0$ and $w_1 = \pi$. Starting from $w_1 = 0$, the value of u_1 changes in a monotonic way until the curve reaches $w_1 = \pi$, or returns to $w_1 = 0$. There are several possible cases of this: (1) $\partial H/\partial u_1$ has no roots within the real interval $0 \leq w_1 \leq \pi$, then the variable w_1 increases also monotonically (Fig. 1, Curve I.). (2) $\partial H/\partial u_1$ has in the above interval *one* simple root at $w_1 = w_1^\circ$; then the curve turns back at this point (Curve

II.). (3) $\partial H/\partial u_1$ has *two* roots or one double root (Fig. 2, Curve III.).

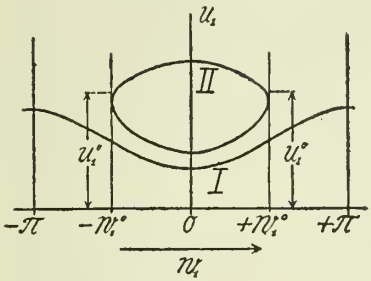

Fig. 1.

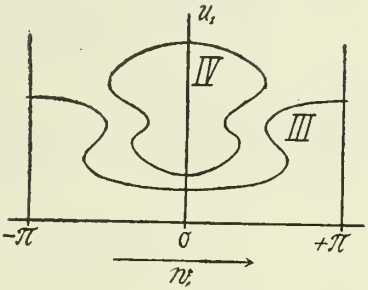

Fig. 2.

(4) $\partial H/\partial u_1$ has three roots (Curve IV.), and so on.[1]

The question now arises as to whether it is possible to realize by a proper choice of the constants α the cases of the curves I. and II. I have not succeeded in answering this question generally for any functions H_1 and b, but in every special case the investigation is carried out easily.

§ 5. Theory of Conditionally Periodic Motions (Continued).

We will discuss the above question in two instances typical for practical problems.

(*a*) Let equation (17′) be given in the form

$$-\frac{1}{2(u_1+u_2)^2}+\frac{\beta}{2}(u_1+u_2)^2\cos w_1 = \alpha,$$

where β is a constant. According to (19) a turning point can only appear when condition

$$\frac{1}{(u_1+u_2)^3}+\beta(u_1+u_2)\cos w_1^0 = 0$$

is fulfilled.

The elimination of u_1+u_2 from these two equations yields for the position of the turning point

$$\cos w_1^0 = -\frac{\alpha^2}{\beta}. \tag{20}$$

We thus arrive at the result: If $a^2 > |\beta|$, there exists no turning point and the curve is of the type I., running monotonically from $w_1 = 0$ to $w_1 = \pi$. If $\alpha^2 < |\beta|$ there exists one and only one turning point between 0 and π, for $\cos w_1^2$ by (20) is uniquely determined for every value of α. Therefore we have the curve of type II. The cases III. and IV. cannot be realized by any choice of α.

[1] If the assumption, that u_1 is real for $w_1 = 0$, is omitted, there exist still two other types of curves for *one* and *two* roots of $\partial H/\partial u_1$.

(*b*) Let the Hamiltonian function be expressed by

$$H = -\frac{1}{2(u_1 + u_2)^2} - \omega u_1 + 2\beta\sqrt{u_1}\cos w_1 = \alpha,$$

and let β be a small quantity and u_1 be restricted also to small values only, ω being a positive constant.

Condition (19) for the turning point yields

$$\frac{1}{(u_1 + u_2)^3} - \omega + \frac{\beta}{\sqrt{u_1}}\cos w_1 = 0.$$

We expand both equations in powers of u_1 and confine ourselves to terms of the first order only

$$(21)\qquad \begin{aligned} -\frac{1}{2u_1^2} + \left(\frac{1}{u_2^3} - \omega\right)u_1 + 2\beta\sqrt{u_1}\cos w_1^0 &= \alpha, \\ \left(\frac{1}{u_2^3} - \omega\right) + \frac{\beta}{\sqrt{u_1}}\cos w_1^0 &= 0. \end{aligned}$$

Eliminating u_1 and writing for short $\Omega = 1/u_2^3$, we obtain

$$\cos^2 w_1^0 = -\frac{1}{\beta^2}\frac{1}{\Omega - \omega}\left(\alpha + \frac{1}{2u_2^2}\right).$$

According to condition $0 \leq \cos^2 w_1^0 \leq 1$, which must be satisfied for all real values of w_1^0, we are led to the result (putting $\Omega > \omega$):
In the cases

$$\alpha < -\left[\beta^2(\Omega - \omega) + \frac{1}{2u_2^2}\right] \quad \text{and} \quad \alpha > -\frac{1}{2u_2^2}$$

there does not exist any turning point; in the opposite case

$$-\frac{1}{2u_2^2} \leq \alpha \leq -\left[\beta^2(\Omega - \omega) + \frac{1}{2u_2^3}\right]$$

there is a turning point.

On the contrary, if we put $\Omega < \omega$, the signs $>$ and $<$ in the inequalities must be exchanged. That *no more than one* turning point can exist, results from the following consideration: supposition $u_1 = 0$ would lead to $\alpha = -1/2u_2^2$ and cannot be generally satisfied. Therefore $\sqrt{u_1}$ has always the same sign, and according to equation (21), $\cos w_1^0$ is also restricted to one sign. The limits, within which u_1 is contained, if the case of Curve II. is considered, with both suppositions $\Omega > \omega$ and $\Omega < \omega$ become

$$(23)\qquad 0 \leq u_1 \leq \beta^2.$$

The Curves III. and IV. are not to be obtained in either of our instances. They appear indeed to belong to rare exceptions, and the author did not meet with them in any application studied by him. We can therefore leave these possibilities out of the following considerations. Our result therefore may be stated thus: *in a certain interval of values of the constant α the case of Curve I. is valid, for all other values the case is that of Curve II.*

In the first case the variable w_1 increases without limit, for, according to the canonical equations, velocity w_1 can change its sign only if the condition $\partial H/\partial u_1 = 0$ is fulfilled. The momentum u_1 is then a periodic function of the coördinate w_1 and can be represented by a Fourier-series.

$$u_1 = c_0 + c_1 \cos w_1 + c_2 \cos 2w_1 + \cdots. \tag{24}$$

We shall call this case the "*case of periodicity.*"

In the second case w_1 varies between two fixed limits, or, using an expression of *Charlier*, w_1 performs "a librational motion." We call this behavior therefore the "*case of libration.*" One sees best the analytical character of the function u_1 if he supposes its dependence on w_1 to hold for complex values of w_1 also, and if he accordingly studies the distribution of u_1 in the complex w_1-plane (Fig. 3). In the segment of the real axis between the points $w_1 = -w_1^2$ and $w_1 = +w_1^2$ the variable u_1 has *two* real values, as results from Curve II. (Fig. 1). In the vicinity of the turning points (u_1^0, w_1^0) and $(u_1^0, -w_1^0)$ Curve II. can be approximated by the two parabolæ

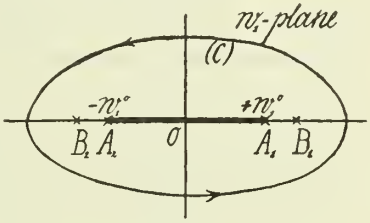

Fig. 3.

$$u_1 - u_1^0 = c\sqrt{w_1 - w_1^0} \quad \text{and} \quad u_1 - u_1^0 = c\sqrt{w_1 + w_1^0},$$

the contact being a simple one by supposition. This means that the function u_1 of the complex variable w_1 has, within the interval $-\pi \leq w_1 \leq +\pi$ of the real axis, *two branch-points* $w_1 = w_1^0$ and $w_1 = -w_1^0$, each one having the exponent $1/2$, so that the totality of all values of this function can be represented by means of a two-sheeted Riemann-surface. If one connects, in the usual way, the two branch-points by a strait cut, function u_1 assumes a set of real values at the lower bank of the cut and another set of real values at the upper bank, which joins continuously the first one at the branch-points. We can, therefore, regard the change of the variable w_1 from the value $-w_1^0$ to $+w_1^0$ and back again *as a circuit around the branch-cut.*

Summarizing we can say: according to the value attributed to the constant α two cases occur. In the *first* case w_1 increases without limit and u_1 is a periodic function of w_1, having the period 2π (*case of periodicity*). In the *second* case w_1 swings monotonically forward from the limit $-w_1^0$ to the limit w_1^0 and backward from w_1^0 to w_1^0, and the analytical behavior of u_1 in the complex w_1-plane can be represented by use of a two-sheeted Riemann-surface (*case of libration*). The circumstances thus agree with those found by Haeckel for the special form of kinetic energy studied by him; we are therefore also justified in naming systems, defined by the Hamiltonian function (17′) or (13) conditionally periodic systems.

By these considerations we have come to a knowledge of the path of the variables u_1 and w_1. We are now to say a few words about the cyclic variables $w_2, w_3, \cdots w_f$. In the usual case of a Hamiltonian function, depending on the momenta quadratically, the cyclic coördinates can increase monotonically only; whereas in our case matters are more complicated, and it is advisable, in order to elucidate them, to use Jacobi's function of action, having here the form

$$W = \int u_1 dw_1 + u_2 w_2 + \cdots + u_f w_f. \tag{25}$$

The equations of motion then are known to be

$$\frac{\partial W}{\partial u_i} = \bar{w}_i \qquad (i = 2, 3, \cdots f),$$

the symbols $\bar{w}_i$ being used to indicate f new constants; or from (25)

$$w_i - \bar{w}_i = -\int \frac{\partial u_1}{\partial u_i} dw_1.$$

In the *first* (periodic) case, when expression (24) for u_1 holds, it follows that

$$w_i - \bar{w}_i = -\frac{\partial c_0}{\partial u_i} w_1 - \frac{\partial c_1}{\partial u_i} \sin w_1 - \frac{1}{2}\frac{\partial c_2}{\partial u_i} \sin 2w_1 + \cdots.$$

The first term of the right side increases monotonically and without limit. To this one-sided increase a periodic change is superposed, having the rhythm of the variable w_1, so that dw_i/dw_1 may have different signs for different values of w_1, from which only the average change of w_i is one-sided. In the special case, where c_0 is independent of u_i ($\partial c_0/\partial u_i = 0$), the average change of w_i vanishes, *i.e.*, we arrive at an oscillation between two fixed limits, or a libration. The period of this libration coincides with the period of the variable w_1, whence we draw the conclusion that this case occurs in so-called "*degenerate*" systems only.

Not very different from these are the conditions in the *second* case, when w_1 performs a librational motion. u_1, and consequently $\partial u_1/\partial u_i$, can then be divided into a *regular* part, having the same value on both banks of the branch-cut of Fig. 3, and into a *branched* part, having opposite signs on the two banks. The contribution of the second part to the integral is permanently positive, while that of the first one is periodic and changes its sign synchronously with w_1. Librational motions result, when the branched part does not depend on u_i. Here, too, this possibility is restricted to cases of degeneration.

It is known that degenerate systems can always be reduced to non degenerate ones with fewer degrees of freedom.[1] We suppose this reduction to be accomplished, and we are then permitted to put aside the possibility of cyclic coördinates, performing a libration. We arrive then at the statement that, though these variables do not always increase monotonically, their eventual fluctuations are of a regularly rhythmical kind, so that their behavior is in agreement with their designation as, "conditionally periodic motions."

§ 6. Introduction of Angular Coördinates.

As one of the chief properties of conditionally periodic motions, we pointed out the possibility of describing them by angular coördinates. We now proceed to show that these coördinates and the corresponding canonical momenta can be found in our more generalized case in just the same way as in the case studied by Haeckel. We shall, moreover, show that everyone of the properties of these variables enumerated in § 2 continues to hold. To avoid the asymmetry of notations coming from the fact that the momentum u_1 is invariable while the other momenta are constant, we shall consider the general case, denoting the coördinates of position by $g_1, g_2, \cdots g_f$, the momenta by $p_1, \cdots p_f$ and the constants of integration by $\alpha_1, \alpha_2, \cdots a_f$ (α_1 meaning the energy of the system). We start by considering the function of action

$$W(q_1, \cdots q_f;\ \alpha_1, \cdots \alpha_f) = \sum_{i=1}^{f} \int p_i(q_i;\ \alpha_1, \cdots \alpha_f)dq_i, \tag{26}$$

in which separation of variables is accomplished. Hence the equations of motion follow by Jacobi's method of integration in the following form

$$\left\{\begin{aligned} t + \beta_1 &= \frac{\partial W}{\partial \alpha_1} = \sum_{i=1}^{f} \int \frac{\partial p_i}{\partial \alpha_1} dq_i, \\ \beta_h &= \frac{\partial W}{\partial \alpha_h} = \sum_{i=1}^{f} \int \frac{\partial p_i}{\partial \alpha_h} dq_i, \quad (h = 2, 3, \cdots f), \end{aligned}\right. \tag{26'}$$

β_i denoting f additional constants.

[1] Cf. P. S. Epstein, l.c., p. 179.

For the behavior of every individual variable g_i we found in § 5 two different possibilities: either the state of the system is a periodic function of the same with the period 2π (*i.e.*, the physical region of variability of q_i equals 2π); or the variable q_i performs a libration, while the corresponding momentum p_i is a function of q_i branched in a certain manner (Fig. 3). In the last case the partial derivatives $\partial p_i/\partial \alpha_h$ evidently belong also to the same branching type. Therefore while q_i performs a libration and comes back to the initial value (resp. while q_i increase by 2π), the integral

$$s_{ih} = \int \frac{\partial p_i}{\partial \alpha_h} dq_i, \qquad (i, h = 1, 2, \cdots f), \tag{27}$$

changes by the "modulus of periodicity"

$$w_{ih} = \oint \frac{\partial p_i}{\partial \alpha_h} dq_i. \tag{28}$$

The path of integration, symbolized by the circle at the sign of integration is, in the case of a branched integrand (*libration*), an arbitrary circuit about the branch-cut of the integrand in the complex q_i-plane which, however, is not permitted to include other singularities of the integrand.[1] In the case of unlimited increase of q_i (*periodicity*) it is the real path of integration from 0 to 2π.

On the other hand, if one inverts equation (27) and regards the variable q_i as a function of s_{ih}, q_i turns out as a *periodic function* of this quantity with the period ω_{ih}.[2] This kind of dependence makes it possible to introduce new variables by the relations

$$\frac{\partial W}{\partial \alpha_1} = t + \beta_1 + \frac{1}{2\pi} \sum_{i=1}^{f} \omega_{i1} w_i,$$
$$\frac{\partial W}{\partial \alpha_h} = \quad \beta_h \quad = \frac{1}{2\pi} \sum_{i=1}^{f} \omega_{ih} w_i,$$

due to Weierstrass, in such a way, that the state of the system becomes periodic with respect to the same, having the period 2π. These are the angular coördinates looked for, which, as follows from equations (29), are in this case also linear functions of time.

Also the canonical momenta, corresponding to the angular coördinates, are expressed in the same way as in Haeckel's case. For it was shown by the author (l.c.), that there they are given by the expressions

$$u_i = \frac{1}{2\pi} \oint p_i dq_i, \qquad (i = 1, 2, \cdots f), \tag{30}$$

[1] Such an integral was called by Riemann a "*complete*" integral.

the symbol of integration having the same meaning as in (28). These equations can be regarded as f simultaneous relations between the constants $\alpha_1, \alpha_2, \cdots \alpha_f$, on which the momenta p_i are dependent, and can be resolved with respect to these constants. It follows that

$$\alpha_i = \alpha_i(u_1, u_2, \cdots u_f), \qquad (i = 1, 2, \cdots f), \tag{31}$$

where the first of these expressions gives the Hamiltonian function as we shall see immediately.

We now multiply the equations (29) by $\partial\alpha_h/\partial u_k$ respectively and add all these equations

$$\sum_{h=1}^{f} \frac{\partial W}{\partial \alpha_h} \cdot \frac{\partial \alpha_h}{\partial \alpha_k} = \frac{1}{2\pi} \sum_{i=1}^{f} w_i \sum_{i=1}^{f} \omega_{ih} \frac{\partial \alpha_h}{\partial u_k}. \tag{32}$$

The path of integration in the formulæ (28) and (29) can be regarded as a fixed one, independent of the constants α_i, from which results:

$$\omega_{ih} = 2\pi \frac{\partial u_i}{\partial \alpha_h}.$$

The second sum on the right of (32) hence becomes

$$\sum_{h=1}^{f} \frac{\partial u_i}{\partial \alpha_h} \cdot \frac{\partial \alpha_h}{\partial u_k} = \frac{\partial u_i}{\partial u_k},$$

while the left side is reduced to $\partial W/\partial u_k$:

$$\frac{\partial W}{\partial u_k} = \sum_{i=1}^{f} \frac{\partial u_i}{\partial u_k} w_i.$$

The quantities u_i are independent, all derivatives vanish, therefore, with the exception of the case $i = k$, in which the derivative becomes equal to 1. From the sum on the right there remains the single term w_i. We can therefore draw the following conclusion: *if in the expression* (26) *of the Hamiltonian function, the constants α_i are replaced by the new constants u_i by means of equations* (31), *the following relations follow*

$$\begin{cases} W = W(q_1, \cdots q_f;\ u_1, \cdots u_f), \\ p_i = \dfrac{\partial W}{\partial q_i}, \qquad w_i = \dfrac{\partial W}{\partial u_i}. \end{cases} \tag{33}$$

According to § 2 these equations give the analytical expression of a contact-transformation, arranging the transition from the coördinates u_i, w_i. It results from this, that these latter variables are *canonical coördinates* of the system. We have already pointed out, that the coordinates w_i are linear functions of time, and that the momenta are constants. Lastly, the first of relations (31) shows, that the energy α_1 is

expressed by the momenta u_i only, and does not depend on the variables w_i.

§ 7. Computation in the Case of Periodicity.

The carrying through of the calculations given in § 6 generally presents difficulties. In the special case, however, where the second term of the Hamiltonian function is small compared with the first one (which is always the case in the theory of perturbations), it can be carried out by successive approximation. We shall show this first to be true in the case of periodicity. Returning to the notations of § 4, let the original coördinates be u_i, w_i. By contact-transformation (15) we arrive at the system u_i', w_i', while u_i'', w_i'' are the angular variables.

To begin with, we shall show how the momenta u_i' can be expressed by the new ones u_i'' and how the energy α can be calculated in terms of the momenta u_i''. We shall however restrict ourselves to the degree of precision required for the applications of Part II. (dealing with the theory of dispersion).

The cyclic variables w_2', w_3', $\cdots w_f'$ are disposed of in a few words. Since librational motions are excluded (cf. the end of § 4), the integration in (30) goes from 0 to 2π, and the momenta u_i' being constant, this equation immediately yields

$$u_i' = u_i'', \qquad (i = 2, 3, \cdots f). \tag{34}$$

This result remains true for the case of librations dealt with in the next paragraph.

We now turn to the non-cyclic variable w_1' and consider the case in which the corresponding momentum u_1' is periodic. The limits of integration of equation (30) are again 0 and 2π; if we introduce for u_i' expression (24), there follows

$$u_i' = c_0$$

and

$$u_1' = u_1'' + c_1 \cos w_1' + c_2 \cos 2w_1' + \cdots, \tag{35}$$

where the coefficients c_i depend on the constants u_1'', $\cdots$ u_f''.

We now make use of our supposition that the quantity b' in the Hamiltonian function (17′) is small compared to H_1'. This means that even H_1', neglecting the second term, gives a certain approximation to the real motion, at least for short times, and that momentum u_1'' differs only by a small quantity of the order b'/H_1' from the momentum u_1' defined by the first term

$$u_1' = u_1'' + \delta, \tag{36}$$

where

$$\delta = c_1 \cos w_1' + c_2 \cos 2w_1' + \cdots. \tag{36'}$$

We suppose functions H_1' and b' in the vicinity of $u_1' = u_1''$ to be developable in powers of the small quantity δ

$$(37)\qquad \begin{cases} H_1'(u_1') = H_1'(u_1'' + \delta) = a_0 + a_1\delta + a_2\delta^2 + \cdots, \\ b'(u_1') = b'(u_1'' + \delta) = b_1 + b_2\delta + b_3\delta^2 + \cdots, \end{cases}$$

where we put for short

$$(38)\qquad a_n = \frac{1}{n!}\left(\frac{\partial^n H_1'}{\partial u_1'^n}\right)_{u_1'=u_1''}; \qquad b_{n+1} = \frac{1}{n!}\left(\frac{\partial^n b'}{\partial u_1'^n}\right)_{u_1'=u_1''}$$

The indices are so chosen as to indicate the order of magnitude of the term in question.

When inserted in equation (17) this leads to

$$a_0 + a_1\delta + a_2\delta^2 + \cdots + (b_1 + b_2\delta + \cdots)\cos w_1' = \alpha.$$

We substitute series (36′) for δ and arrange the expression according to cosines of the multiples of w_1':

$$\left(a_0 - \alpha + \frac{a_2c_1}{2} + \frac{b_2c_1}{2} + \cdots\right) + (a_1c_1 + b_1 + \cdots)\cos w_1'$$
$$+ \left(\frac{a_2c_1}{2} + \frac{b_2c_1}{2} + a_1c_2 + \cdots\right)\cos 2w_1' + \cdots = 0.$$

This relation being valid for any value of w_1', the coefficients must vanish individually, and this yields an infinite series of equations for the calculation of $c_1, c_2, c_3, \cdots$ and α. Restricting ourselves to terms of the first and second order, we have

$$(39)\qquad c_1 = -\frac{b_1}{a_1}, \qquad c_2 = \frac{b_1}{2a_1^3}(a_1b_2 - a_2b_1),$$

$$(40)\qquad \alpha = a_0 + \frac{b_1}{2a_1^2}(a_2b_1 - a_1b_2) + \cdots.$$

The problem of expressing α and u_1' in terms of u_1'' is thus solved, but there remains that of expressing coördinates w_i' in terms of the angular variables w_i'' and of the corresponding momenta u_i''. According to § 6 we have to apply contact-transformation (33), while Jacobi's function (26) assumes the form

$$W = \int u_1' dw_1' + \sum_{i=2} u_i'' w_i',$$

or by use of formulæ (34) and (36)

$$(41)\qquad W = \sum_{i=1} u_i'' w_i'' + c_1 \sin w_1' + c_2 \sin 2w_1' + \cdots.$$

Contact-transformation (33) yields besides the relations (34) and (36),

already known to us, the new ones

$$(42)\quad w_i'' = w_i' + \frac{\partial c_1}{\partial u_i''}\sin w_1' + \frac{1}{2}\frac{\partial c_2}{\partial u_i''}\sin 2w_1' + \cdots \qquad (i = 1, 2, \cdots f),$$

whence by inversion (neglecting terms of the second order)

$$(43)\qquad w_i' = w_i'' - \frac{\partial c_1}{\partial u_i''}\sin w_1''.$$

The transformations, hitherto used, are well fitted for studying the character of the motion, but they have the disadvantage of treating the pair of coördinates w_1, u_1 in a different way from the rest. By this an asymmetry is carried into the final formula which is not justified by physical reasons.

For kinematical and dynamical conclusions it obviously does not matter what kind of coördinates are used in describing the motion, but this is not so for the theory of quanta: as soon as quantum conditions are involved an arbitrary procedure may have dangerous consequences. The asymmetry should therefore be avoided, and this is easily accomplish The asymmetry should therefore be avoided, and this is easily accomplished by use of a third transformation which is the inverse of (15):

$$(44)\qquad \begin{cases} W = u_1''(m_1 w_1''' + \cdots + m_f w_f''') + \sum\limits_{i=2} u_i'' w_i''', \\ \dfrac{\partial W}{\partial w_i'''} = u_i''', \qquad \dfrac{\partial W}{\partial u_i''} = w_i''. \end{cases}$$

The formulæ for the direct transition from u_i, w_i to u_i''', w_i''' can be drawn from (15), (35), (36), (42) and (44). Using the abbreviations

$$(45)\quad \begin{aligned} -\vartheta &= m_1 w_1 + m_2 w_2 + \cdots + m_f w_f, \\ -\varphi(u_1''', \cdots u_f'''; \vartheta) &= c_1 \sin\vartheta + \tfrac{1}{2}c_2 \sin 2\vartheta + \tfrac{1}{3}c_3 \sin 3\vartheta + \cdots, \end{aligned}$$

where coefficients c_i are to be regarded as functions of the new constants u_i'''. The formulæ looked for are found to have the perfectly symmetric form

$$(46)\quad u_i = u_i''' + \frac{\partial\varphi}{\partial w_i}, \qquad w_i''' = w_i + \frac{\partial\varphi}{\partial u_i'''}, \quad (i = 1, 2, \cdots f).$$

These equations form a contact-transformation, which may be written thus

$$(47)\qquad \begin{cases} W = \sum\limits_{i=1}^{f} u_i''' w_i + \varphi(u_1''', \cdots u_f'''; \vartheta), \\ \dfrac{\partial W}{\partial u_i'''} = w_i''', \qquad \dfrac{\partial W}{\partial w_i} = u_i. \end{cases}$$

In fact this transformation was introduced by Poincaré and adopted by Whittaker, the form of the function φ being left provisionally indeterminate. Whittaker's results agree completely with the formulæ of this paragraph, but assumption (45) for the form of function φ is made by him quite arbitrarily, and it does not appear from his treatment whether this assumption is always admissible; whereas from our treatment it follows that this assumption is possible for a limited region of values of the constant α only, but that it is necessary in this region.

Equations (39) and (40) continue to hold also if transformation (44) is applied, a_n and b_n now meaning

$$(48)\qquad \begin{cases} a_n = \dfrac{1}{n!}\left[\left(m_1\dfrac{\partial}{\partial u_1} + \cdots + m_f\dfrac{\partial}{\partial u_f}\right)^n H_1\right]_{u_i=u_i'''}, \\ b_{n+1} = \dfrac{1}{n!}\left[\left(m_1\dfrac{\partial}{\partial u_1} + \cdots m_f\dfrac{\partial}{\partial u_f}\right)^n b\right]_{u_i=u_i'''}. \end{cases}$$

§ 8. Computation in the Case of Libration.

The problem becomes more complicated than in the last paragraph if the variable w_1' performs librational motions. Theoretically it is always possible to represent the integrand of (25) in terms of a single variable, introducing u_1' by means of the equation of energy (17′):

$$w_1' = \arccos\frac{\alpha - H_1'(u_1)}{b'(u_1)},$$

whence

$$\int u_1' dw_1' = \int u_1' d \arccos\frac{\alpha - H_1'(u_1')}{b'(u_1')}.$$

But practically this way turns out to be very tedious. In computations of moderate precision one succeeds much more quickly by using a method explained in the following lines which forms an important part of our communication. But I have had no experience as to which procedure is more convenient in calculations of great accuracy.

To make clear the idea of our method, we shall consider the special form, under which the case of libration appears both in the theory of three bodies and in the theory of dispersion (keeping in mind that the scope of application of this method is a much larger one). In the problems mentioned, librations occur only when the equation of energy (17′) assumes the special form

$$(49)\qquad H_1' + 2\beta\sqrt{u_1'}\cdot\cos w_1' = \alpha,$$

where u_1' has a small numerical value and H_1' and β are functions developable in powers of u_1', which may depend on the constants $u_2', \cdots u_f'$ as well.

We make use of the expansion

$$(50)\qquad \begin{cases} H_1'(u_1') = a_0 + a_1u_1' + a_2u_2'^2 + \cdots, \\ \beta(u_1') = \beta_1 + \beta_2u_1' + \beta_3u_1'^2 + \cdots, \end{cases}$$

where β is not equal to zero. It follows from the equation of energy that:

$$(51)\qquad (a_0 - \alpha + 2\beta_1\sqrt{u_1'}\cos w_1' + a_1u_1') + (2\beta_1\sqrt{u_1'}\cos w_1' + a_2u_1')u_1' + \cdots = 0.$$

This series converging more or less rapidly, we can provisionally neglect terms of higher order in u_1 in order to get an approximate value of u_1 by solving the remaining equation, and then build up an expansion of u_1 by taking into account the neglected terms one after another. We have seen in § 5, that, looked at as a function of the complex variable w_1, the momentum u_1 has two branch-points with the exponent 1/2. *The point of our method is to form the expansion in such a way that every individual term of it shall be of this type of branching.*

We easily arrive at such an expansion in the following way: We denote the totality of all terms of relation (51), with the exception of the first parenthesis, by Δ

$$(52)\qquad \Delta = (2\beta_2\sqrt{u_1'}\cos w_1 + a_2u_1')u_1' + \cdots$$

and thus write that equation in the form

$$a_0 - \alpha + \Delta + 2\beta_1\sqrt{u_1'}\cos w_1' + a_1u_1' = 0,$$

which can be formally solved for $\sqrt{u_1}$

$$(53)\qquad \sqrt{u_1'} = -\frac{\beta_1}{a_1}\cos w_1' \pm \frac{1}{a_1}\sqrt{\beta_1^2\cos^2 w_1' + a_1(\alpha - a_0) - a_1\Delta}.$$

If squared, and at the same time expanded in powers of the small quantity Δ, this equation gives

$$(54)\qquad u_1' = \frac{1}{a_1^2}\left\{\Phi + \beta_1^2\cos^2 w_1' \mp 2\beta_1\sqrt{\Phi}\cos w_1' - a_1\left(1 \mp \frac{\beta_1\cos w_1'}{\sqrt{\Phi}}\right)\Delta \pm \frac{1}{4}\frac{a_1^2\beta_1\cos w_1'}{\Phi^{312}}\Delta^2 + \cdots\right\},$$

with the abbreviation:

$$(55)\qquad \Phi = \beta_1^2\cos^2 w_1' + a_1(\alpha - a_0) = \beta_1^2 + a_1(\alpha - a_0) - \beta_1^2\sin^2 w_1'.$$

One gets the first approximation by entirely neglecting the quantity Δ

$$(56)\qquad u_1' = \frac{1}{a_1^2}\{\Phi + \beta_1^2\cos^2 w_1' \mp 2\beta_1\sqrt{\Phi}\cos w_1'\},$$

$$(56')\qquad \sqrt{u_1'} = -\frac{\beta_1}{a_1}\cos w_1' \pm \frac{1}{a_1}\sqrt{\Phi}.$$

This approximation is sufficient for treating the case given in Communication III. The following point in these equations is remarkable: u_1' being real by its physical meaning, $\sqrt{\Phi}$ cannot become imaginary, and consequently $\sqrt{u_1'}$ always remains real also. It follows from this that u_1' is always positive and never passes through the value $u_1' = 0$.

The *second* approximation results, if the first one is carried into the correction term of the first order with respect to Δ, and if correction terms of higher order are neglected. To obtain the *third*, the second must be carried into the terms of first order and the first into those of second order, and so on. In any case u_1 is represented by a series, expanded in integer powers of $\sqrt{\Phi}$, and this latter function $\sqrt{\Phi}$ is evidently of the type of branching desired.

At every step of approximation the momentum acquires the form

$$u_1' = F(\cos w_1', \sqrt{\Phi}), \tag{57}$$

where F is a *rational* function of the two arguments. Hence, according to (30), momentum u_1'', corresponding to the angular variable results in the form

$$u_1'' = \frac{1}{2\pi} \oint F(\cos w_1', \sqrt{\Phi}) dw_1'. \tag{58}$$

The path of integration in the complex w_1'-plane is here a circuit around the two branch-points A_1, A_2 of the exact function u_1' which do not coincide exactly, but only approximately with those (B_1, B_2) of the square root $\sqrt{\Phi}$ (Fig. 3[1]). A closed curve (c), however, which embraces the first two branch-points, if plotted in a suitable way, encloses also the latter two. We can therefor regard (58) at any degree of approximation as a "complete" integral, encircling the branch-cut of function $\sqrt{\Phi}$, which means a considerable simplification of the considerations.

Equation (58) gives us therefore u_1'' as a function of energy α. By inversion (*e.g.*, using successive approximation) the looked-for dependence of energy on the momentum u_1'' is found. For the purpose of Communication II., the first approximation given by equation (56) is sufficient: the part which is rational with respect to $\cos w_1'$ yields no contribution to the integral, and this reduces to

$$u_1'' = \frac{\beta_1}{\pi a_1^2} \oint \sqrt{\beta_1^2 + a_1(\alpha - a_0) - \beta_1^2 \sin^2 w_1'} \cdot d \sin w_1'. \tag{59}$$

Account is already taken in this expression of the double sign of the square root, because, proceeding along the path of integration, the sign changes automatically at the moment of passing from the lower to the

[1] We recall that in § 5 the accents at the letters were dropped.

upper bank of the branch cut. We shall agree, that u_1'' is positive, which is true, if, β_1 being positive, we attribute to the roots (56) and (56′) the lower sign on the lower bank of the branch cut[1]. The integration is easily accomplished and yields:

$$u_1'' = \frac{\beta_1^2 + a_1(\alpha - a_0)}{a_1^2}, \tag{60}$$

from which the expression of energy looked for is obtained in the form

$$\alpha = a_0 - \frac{\beta_1^2}{a_1} + a_1 u_1''. \tag{61}$$

Without entering into the particulars of the deduction, we will give the second approximation of the energy also:

$$\begin{aligned} \alpha = a_0 - \frac{\beta_1^2}{a_1} - \frac{\beta_1^3}{a_1^4}(2a_1\beta_2 - a_2\beta_1) + a_1 u_1'' \\ - 4\frac{\beta_1}{a_1^4}(a_1\beta_2 - a_2\beta_1)u_1'' + \frac{5a_2}{8a^7}u_1''^2. \end{aligned} \tag{62}$$

It must be kept in mind that, for the momenta u_2', u_3', $\cdots$ u_f' corresponding to cyclic coördinates, relations (34) remain valid

$$u_i' = u_i'', \qquad (i = 2, 3, \cdots f) \tag{34}$$

and that the quantities a_0, α, β_1 are expressed in terms of the constants u_2', u_3', $\cdots$ u_f'. By (61) or by (62) the energy α is therefore given as a function of the momenta $u_1''(i = 1, 2, \cdots f)$.

In order to pass from the variables w_i', u_i' to the angular coördinates w_i'', we make use again of the contact-transformation (33). The function of action

$$W = \int u_1' dw_1' + \sum_{i=2}^{f} u_1' w_1'$$

is now to be expressed in terms of the variables u_i'' and w_i' which yields according to (56), (61) and (34):

$$\begin{aligned} W = \sum_{i=2}^{f}{}_i\, u_i'' w_i' + \frac{\beta_1^2}{a_1}\cos 2w_1' \\ + \frac{2\beta^1}{a_1^2}\int \sqrt{a_1^2 u_1'' - \beta_1^2 \sin^2 w_1'}\cdot d \sin w_1', \end{aligned} \tag{63}$$

$$w_i'' = \frac{\partial W}{\partial u_i''}, \qquad u_i' = \frac{\partial W}{\partial w_i'}. \tag{64}$$

[1] If β_1 is negative, in all following formulæ of this paragraph the sign of β_1 must be changed.

From the first of the equations (64) there follows for $i = 1$

$$w_1'' = w_1' - \arcsin\left(\frac{\beta_1}{a_1\sqrt{u_1''}}\sin w_1'\right),^1 \tag{65}$$

or

$$\frac{\beta_1}{a_1\sqrt{u_1'}}\sin w_1' = -\sin w_1''\cdot\cos w_1' + \cos w_1''\cdot\sin w_1',$$

whence

$$\begin{cases} \sin w_1' = -\dfrac{a_1\sqrt{u_1''}\,\sin w_1''}{\sqrt{\beta_1^2 + a_1^2u_1'' - 2a_1\beta_1\sqrt{u_1''}\cos w_1''}}, \\[2ex] \cos w_1' = \dfrac{\beta_1 - a_1\sqrt{u_1''}\cos w_1''}{\sqrt{\beta_1^2 + a_1^2u_1'' - 2a_1\beta_1\sqrt{u_1''}\cos w_1''}}. \end{cases} \tag{66}$$

Introducing these expressions into equation (56′) and taking into account our convention with respect to the sign, we have

$$\sqrt{u_1'} = -\frac{1}{a_1}\sqrt{\beta_1^2 + a_1^2u_1'' - 2a_1\beta_1\sqrt{u_1''}\cos w_1''}. \tag{67}$$

Our relations (66) assume therefore the form

$$\begin{aligned} \sqrt{u_1'}\sin w_1' &= \sqrt{u_1''}\sin w_1'', \\ \sqrt{u_1'}\cos w_1' &= -\frac{\beta_1}{a_1} + \sqrt{u_1''}\cos w_1''. \end{aligned} \tag{68}$$

If β_1 is not positive, but negative, the upper sign of formulæ (56) and (56′) must be chosen. Then in equations (59), (65), (66) the constant β_1 and in (67) the square root also undergo a change of sign, whereas the final formulæ remain unchanged.

By means of the transformation (63), (64) it is also easy to express the variables w_2', w_3', $\cdots w_f'$ in terms of the angular coördinates. This, however, is not necessary for the applications of Communication II.

By the special form of the energy equation (49) coördinate u_1' is really emphasized so that the asymmetry involved in contact-transformation (15) is physically justified. A further transformation of these equations is therefore superfluous in the case of this paragraph.

§ 9. Whittaker's Modification of Delaunay's Method.

In our introduction we have already mentioned an investigation on the theory of perturbations, due to Whittaker. The chief assumption of his method consists in using expansion (45) for function φ of the

[1] We write $(-)$, making use of the abitrariness of sign at $\sqrt{u_2''}$. The sign of $\sqrt{u_1'}$ being negative according to (56′), we shall ascribe to $\sqrt{u_1''}$ also the negative sign.

contact-transformation (47). As we showed in § 7 this amounts to supposing the momentum u_1' to be always developable into the Fourier-series

$$u_1' = c_0 + c_1 \cos w_1' + c_2 \cos 2w_1' + \cdots.$$

Whittaker thus makes the assumption that momentum u_1' is always a periodic function of the variable w_1', whereas we showed in §§ 4, 5, that besides this possibility there exists the other one of librational motion and that in every individual case it depends on the numerical values of the constants whether the one or the other alternative is obtained. We see from these facts, *that Whittaker's method exhausts the problem not totally but only in part.*

That the case of libration is by no means of minor importance we conclude from its occurring both in the problem of three bodies and in the theory of dispersion (cf. Communications II. and IV.). Using Whittaker's procedure of approximation uncritically one always runs the risk of applying expression (40) outside the limits of its validity, for these limits cannot be determined from that procedure, but only from general considerations such as those of our §§ 4, 5. We will discuss the simple instance of the physical pendulum in order to show to what mistakes one is liable to fall a victim.

Let l be the reduced length of the pendulum in its mass, α the energy, g the acceleration of the field of gravitation, and ϑ the angle of displacement measured from the center of oscillation. Then the energy equation is

$$p^2 + \mu \cos \vartheta = C, \tag{69}$$

putting, for short, $\mu = 2m^2gl^3$ and $C = 2ml^2\alpha$. According to (30) the momentum corresponding to the angular coördinate is then

$$u = \frac{1}{2\pi} \oint p d\vartheta = \frac{1}{2\pi} \oint \sqrt{C - \mu \cos \vartheta \, d\vartheta}. \tag{70}$$

Even in this simplest case the two paths of integration, mentioned in §§ 4, 5 must be discriminated:

1. $C > \mu$, *i.e.*, the pendulum swings over and performs a rotational motion. This is the *case of periodicity*, for p is then a periodic function of the angle ϑ and the integration must be extended from 0 to 2π. We reduce the elliptic integral (70) to its normal form

$$u = \sqrt{\frac{C + \mu}{\pi}} \int_0^{2\pi} \sqrt{1 - k^2 \sin^2 \frac{\vartheta}{2}} \frac{d\vartheta}{2}, \quad k = \sqrt{\frac{2\mu}{C + \mu}}.$$

With the assumptions made k is less than unity and the integral by a

usual method becomes

$$u = \sqrt{C + \mu}[1 - \tfrac{1}{4}k^2 + \cdots],$$

whence

$$C = u^2 + \frac{\mu^2}{4u^2} + \cdots. \tag{71}$$

2. $C < \mu$, this is the more usual *case of the librational motion* or oscillation of the pendulum. As shown in § 6 the integral must then be taken in the complex plane around the branch cut of the integral. The modulus k is larger than 1, and it is advisable to transform the integral, introducing a new variable by the substitution $k \sin \vartheta/2 = \sin \psi$:

$$u = \frac{C + \mu}{\pi \sqrt{2\mu}} \int_0^{2\pi} \frac{\cos^2 \psi d\psi}{\sqrt{1 - \frac{1}{k^2} \sin^2 y}} = \frac{C + \mu}{\sqrt{2\mu}} \left[1 + \frac{1}{8k^2} + \cdots \right]$$

and

$$C = \sqrt{2\mu}\, u \left(1 - \frac{u}{8\sqrt{2\mu}} + \cdots \right) - \mu. \tag{72}$$

We have therefore in the case $C > \mu$ an expansion in decreasing powers of u^2, in the case $C < \mu$ one in increasing powers of u. It is here quite evident that the case of libration should not be overlooked and that applying the expansion in decreasing powers to the case $C < \mu$ is not permissible. In most problems of the theory of perturbations the circumstances are not so transparent and must be carefully analyzed.

We admit that this case, discussed for illustration because of its simplicity in calculations, does not entirely correspond to the conditions of the perturbation theory: librational motion only occurs when the term $\mu \cos \vartheta$ is no longer small compared with p^2 but has the same order of magnitude. One can therefore scarcely regard the oscillation of the pendulum in the field of gravity as a perturbation of the rotational motion without field. There are however enough cases in the theory of perturbations in which a very small term produces a decisive change of the analytical character of the whole problem. We have seen in § 4 that the derivative $\partial b/\partial u_1$ discriminates between periodicity and libration. Now just in the special case studied in § 8, we have $b = 2\beta\sqrt{u_1}$ and $\partial b/\partial u_1 = \beta/\sqrt{u_1}$ (neglecting small terms). Thus, if u_1 has a very small numerical value, a very small perturbational term may have a numerically large derivative and may exercise considerable effect.

10. Aspects of the Theory of Quanta Opened up by this Method.

In our preceding considerations we tacitly supposed that the undisturbed motion, given by the Hamiltonian function H_1 of equation

(12), does not belong to the class of "*degenerate*" motions. With this supposition we arrived at the conclusion *that in passing from one approximation to the next one the momenta, suitable for quantization according to* (11), *change by small correction terms only.*

We will now drop this restriction and extend our considerations to degenerate systems. The property of such systems which is most important to us[1] is the existence of one or several commensurabilities between the *average motions* (10), having the form

$$k_1\Omega_1 + k_2\Omega_2 + \cdots + k_f\Omega_f = 0, \tag{73}$$

where $k_1, k_2, \cdots k_f$ are whole numbers. The number of existing commensurabilities we shall call the "*degree of degeneration.*" The highest degree possible is obviously $f - 1$, only one of the variables w_i remaining independent. This highest degree of degeneration is reached by periodic motions.

Among the terms of perturbation function (12) such may occur which have just the argument

$$k_1w_1 + k_2w_2 + \cdots + k_fw_f,$$

where by k_i are denoted the same numbers as in (73). Such terms can properly be called "*degenerate terms.*" The special properties of these degenerate terms appear, when transformation (16) is applied, for the canonical equations yield

$$\frac{\partial H_1}{\partial u_1'} = w_1' = k_1\Omega_1 + \cdots + k_f\Omega_f = 0. \tag{74}$$

Function H_1 is thus altogether independent of u_1' and is therefore a constant, all other arguments ($u_2', u_3', \cdots u_f'$) of this function being constant. We can combine this constant with the energy and write

$$\alpha' = \alpha - H_1, \tag{75}$$

whence (17′) assumes the simpler form

$$b(u_1) \cos w_1 = \alpha'. \tag{76}$$

Now in this equation the term $b(u_1) \cos w_1$ is no longer a small correction term, but the only variable term. This circumstance requires *that a degenerate term produces not a small correction of the special coördinates justified for quantization, but a decisive change of the same.*

For the convenience of the following communications we shall put together the formulæ for the treatment of degenerate terms. The methods used in §§ 7, 8 cannot be applied here, and we will follow the

[1] Cf. P. S. Epstein, Ann. d. Phys., *51*, p. 179, 1916.

procedure briefly mentioned in the beginning of § 8. We obtain

$$dw_1 = -\frac{\frac{1}{b}\frac{\partial b}{\partial u_1}du_1}{\sqrt{b^2 - \alpha'^2}} \tag{77}$$

and according to (30) and (34)

$$u_1' = -\frac{\frac{1}{2\pi}\oint \frac{1}{b}\frac{\partial b}{\partial u_1}du_1}{\sqrt{b^2 - \alpha'^2}}, \qquad u_i' = u_i, \quad (i = 2, 3, \cdots f). \tag{78}$$

By means of these relations α_1 must be determined in terms of the quantities u_i'. The angular coördinates then result from the contact-transformation

$$W = \int u_1 dw_1 + \sum_{i=2}^{f} u_i' w_i$$

$$w_i' = \frac{\partial W}{\partial u_i'}, \qquad u_i = \frac{\partial W}{\partial w_i},$$

where u_1 must be regarded as a function of u_i' and w_1 given by equations (76) and (78). In this manner we obtain

$$\begin{cases} w_1' = \int \frac{\partial u_1}{\partial u_1'}dw_1, \\ w_i' = w_i + \int \frac{\partial u_1}{\partial u_i'}dw_1, \qquad (i = 2, 3, \cdots f). \end{cases} \tag{79}$$

Taking the logarithm of equation (76), we have

$$\log b = \log \alpha' - \log \cos w_1,$$

and differentiating partially with respect to u_i'

$$\frac{1}{b}\frac{\partial b}{\partial u_1}\frac{\partial u_1}{\partial u_i'} + \frac{1}{b}\frac{\partial b}{\partial u_i'} = \frac{1}{\alpha'}\frac{\partial \alpha'}{\partial u_i'}.$$

In particular: $\partial b/\partial u_1' = 0$, from which

$$\begin{cases} \frac{\partial u_1}{\partial u_1'} = \frac{b}{\frac{\partial b}{\partial u_1}}\frac{1}{\alpha'}\frac{\partial \alpha'}{\partial u_1'}, \\ \frac{\partial u_1}{\partial u_i'} = \frac{b}{\frac{\partial b}{\partial u_i}}\left(\frac{1}{\alpha'}\frac{\partial \alpha'}{\partial u_1'} - \frac{1}{b}\frac{\partial b}{\partial u_i'}\right), \qquad (i = 2, 3, \cdots f). \end{cases} \tag{80}$$

Finally:

$$(81)\qquad \begin{cases} w_1' = \dfrac{1}{\alpha'}\dfrac{\partial\alpha'}{\partial u_1'}\int \dfrac{du_1}{\sqrt{b^2-\alpha'^2}}, \\[2ex] w_i' = w_i + \dfrac{\dfrac{\partial\alpha'}{\partial u_i}}{\dfrac{\partial\alpha'}{\partial u_1'}} w_1' + \displaystyle\int \dfrac{\dfrac{1}{b}\dfrac{\partial b}{\partial u_i'}}{\sqrt{b^2-\alpha'^2}}\, du_1. \end{cases}$$

From the above it appears that the degenerate terms are the most important for determining the coördinates of quantization. It is therefore desirable to have a method of separating them from the perturbation function when the Fourier-expansion of the same is not yet found. To such a separation the following simple consideration leads: Let the perturbation function of equation (8) be formally expressed in terms of the angular coördinates u_i, w_i of the first intermediate motion. Ascribe to the variables u_i, w_i that dependence on time which they possess in the first intermediate motion, *i.e.*: $u_i = \text{const.}$, $w_i = \Omega_i t + \delta_i$. If you form the time average of R_1 for an infinitely long time, you obtain besides the constant term of R_1, independent of the variables w_i, just the sum of the degenerate terms which also are constant, the time dropping out from them according to relation (73).

In this way we write

$$Q = \bar{R}_1 = \lim_{T=\infty} \frac{1}{T}\int_0^T R_1 dt.$$

The time average being independent of the choice of coördinates, we can express Q by any other set of coördinates instead of the angular variables provided that we ascribe to them that dependence on time which they have in the first intermediate motion. In particular the number of coördinates of a degenerate conditionally periodic motion can always be reduced by the degree of degeneration and there can be found a special system of $f - s$ separation variables.[1] Let these special coordinates be denoted by $q_1, q_2, \cdots q_{f-s}$, and the corresponding canonical momenta by $p_1, p_2, \cdots p_{f-s}$, so that $p_i = p_i(q_i;\ \alpha_1, \alpha_2, \cdots \alpha_{f-s})$ where α_i denote the constants of integration. Then the time average (82), according to a theorem due to *Burgers*,[2] can be expressed in the following form, convenient for computation

$$(83)\qquad Q = \bar{R}_1 = \frac{1}{\Delta}\oint\oint\cdots\oint R_1 F dq_1 dq_2 \cdots dq_{f-s},$$

[1] P. S. Epstein, l.c., p. 179.

[2] J. M. Burgers, Verslagen Amsterdam, 1917.

where F and Δ are the two determinants

$$(84)\qquad \begin{cases} F = \left| \dfrac{\partial p_i}{\partial \alpha_h} \right|, \\ \Delta = \left| \oint \dfrac{\partial p_i}{\partial \alpha_h} dq_i \right|. \quad (i, h = 1, 2, \cdots f - s). \end{cases}$$

When the highest degree of degeneration appears the undisturbed motion is a periodic one, and the average for a long time can be replaced by the average for a period. In this case our function Q is identical with Bohr's function Ψ by which the choice of coördinates is determined according to his rules. *Though Bohr's rules are derived from an entirely different point of view, they agree substantially with ours.*[1]

Also in the other cases discussed by Bohr the directions given by him are closely similar to ours. If the undisturbed motion is *non-degenerate*, the effect of a *very small* perturbation depends essentially on the aperiodic term (*i.e.*, the constant term, independent of $w_1, \cdots w_f$); for according to formulæ (40) and (61) all other terms yield changes of energy, containing the small quantity b_1 (resp. β_1) quadratically. This aperiodic term, if quantities of the second order are neglected, must be expressed by the original coördinates of the undisturbed motion so that the changes in the motion produced by the perturbation need not be investigated at all in this case.

In motions *entirely or partially degenerate* the degenerate terms must be discarded one after another in the way described. If we denote by s the degree of degeneration, the problem is reduced to a non-degenerate one in s steps.[2] Therefore every motion to which the general theory of this paper is applicable is in principle liable to rigorous quantization; and in this consists the chief difference between our view and that of Bohr, which makes us expect rigorous quantization to be impossible in most cases, and therefore, spectral lines to become diffuse. It is, however, to be pointed out that the convergence conditions of the procedure become extremely unfavorable if several degenerate terms exist, so that the determination of quantization coördinates may become impracticable, owing to difficulties of computation. But in any case much is already

[1] We believe that in the text of this paragraph general and unambiguous directions as to how such terms are to be treated are for the first time given. Bohr's (l.c., p. 55) assertion that the integral must be taken between the limits θ and 2π of his variables βi appears to be a mistake, for generally βi has not the dimension of an angle. In discussing instances Bohr and Kramers make use of special artificial methods, applicable to the cases in question only.

[2] The case may occur that the disturbed motion is also degenerate, having a degree of degeneration S ($< s$). Then the reduction is accomplished in $s - S$ steps. This involves no change in our conclusions, a degenerate system being formally reducible to a non-degenerate one of fewer degrees of freedom.

gained if a method is known by which the treatment can be attempted generally, and carried through in part of the problems. In Communication III. we shall discuss an instance of practical importance for this case: the combined effect of magnetic and electric fields on a hydrogen-like atom.[1]

It is an important question as to whether the resulting coördinates are independent of the arbitrariness, lying in the unrestricted choice of the first intermediate motion and of the order in which the degenerate terms are taken into account. As a matter of fact by a rather simple consideration this independence can at least be made very probable. We shall, however, return to this problem at a later opportunity, and will only mention here that in most of the applications the first intermediate function has a physical meaning: it represents the original or normal motion of the system, while the perturbation function gives the effect of some external source of disturbance. By this the arbitrariness is practically removed. It is moreover obvious that the order of treatment is of no consequence if a greater number of operations is carried through than the number giving the degree of degeneration; the system is no more degenerate at this step of approximation and has therefore one set of separation variables only.

As mentioned in the introduction, the above considerations were worked out in 1917. The lack of agreement with experiment in the case of the helium spectrum caused me however to reject the whole theory.[2] But when Bohr in his above mentioned papers established nearly the same quantization rules which follow from my method, my confidence in it was revived. The scope of this method seems however to be confined to motions of *a single electron in a stationary field.*

I should not like to conclude without expressing my sincere thanks to Mr. I. S. Bowen, who kindly looked through the manuscript of this paper, correcting and smoothing my English style.

CALIFORNIA INSTITUTE OF TECHNOLOGY, September, 1921.

[1] Bohr declared this system to be non-quantitable, l.c., p. 93, 94; Abhandlungen über Atombau, p. XVII, Braunschweig, 1294, if the directions of the two fields enclose a finite angle. But we shall see that it can be rigorously quantized from the point of view of our method.

[2] Cf. P. S. Epstein, Die Naturwissenschaften, p. 230, 1918.

THE ELECTRIC FIELD OF A MAGNETIZED SPHEROID ROTATING ABOUT THE AXIS OF MAGNETIZATION.

By Oswald Rognley.

Synopsis

Electrostatic Potential Due to a Rotating Magnetized Spheroid.—Taking the axis of symmetry as both the axis of rotation and the direction of magnetization, and assuming that the gradient of the potential is at each point equal to $[v \cdot B]/c$ where v is the velocity, B the induction and c the speed of light, formulæ are derived for the potential at any point on the surface or outside of it (a) when the spheroid is insulated and uncharged as a whole and (b) when the axis is kept earthed. In the latter case the change of potential of the surface as a result of reversing the magnetization is equal to $2B\omega b^2/3c$, where ω is the angular speed and $2b$ is the maximum diameter. This change may be measured by the resulting change of potential of a stationary shell surrounding the spheroid. For example, in the case of a long iron cylinder (which is approximately equivalent to a spheroid of the same maximum diameter) of 4 cm. radius, with an induction of 18,000 e.m.u. and revolving 100 times a second, the change of potential of a cylindrical shell of 4.5 cm. radius would be about 0.9 volt.

Experiments on Unipolar Induction are Briefly Discussed to indicate the bearing of the above results upon them.

In a recent paper, Professor W. F. G. Swann[1] has discussed the subject of Unipolar Induction; and as an illustration of the theory developed he has deduced the expression for the potential due to a uniformly magnetized sphere rotating about a diameter parallel to the axis of magnetization. In a later paper[2] he has given an expression for the alteration of potential of an insulated shell surrounding a magnetized sphere when the latter is set in rotation, its axis being earthed; and he has described experiments verifying the expression. Since the magnets used in experimental work are usually of an elongated shape, and since the effect of high permeability would be greater in such a case than in a sphere, it has been thought desirable to extend the problem to the case of a prolate spheroid rotating uniformly about its axis of magnetization.

We shall take as the equation of the spheroid:

$$\frac{x^2}{a^2} + \frac{y^2 + z^2}{b^2} = 1.$$

The magnetization shall be along the axis of x, which shall also constitute the axis of rotation, the direction of rotation appearing clockwise as viewed by an observer looking in the direction of the magnetization. We shall work throughout in Heaviside units.

[1] Swann, Phys. Rev., (2), xv, 365–398, 1920.

[2] Swann, Phys. Rev., (2), xix, p. 381 (1922).

According to the theory as set forth by Professor Swann, the sole agency which is ultimately responsible for the electrostatic distribution is the motional intensity $[v \cdot B]/c$, where v is the velocity of an element of the matter, B the induction, and c the velocity of light. Thus the equations of equilibrium are contained in

$$- \text{Grad } V + \frac{[v \cdot B]}{c} = 0. \tag{1}$$

If ω is the angular velocity this leads to

$$\frac{\partial V}{\partial x} = 0, \qquad \frac{\partial V}{\partial y} = \frac{B\omega y}{c}, \qquad \frac{\partial V}{\partial z} = \frac{B\omega z}{c}.$$

These equations give, for the potential of a point within the spheroid,

$$V = \frac{B\omega}{2c}(y^2 + z^2) + V_0, \tag{2}$$

where V_0 is a constant which obviously represents the potential of the axis and which is arbitrary until we assign some further condition, for example the total charge (zero or otherwise) which the spheroid is to have.

Outside of the spheroid, the potential will satisfy Laplace's equation, and the solution of the problem consists in finding a solution of Laplace's equation which will reduce to (2) on the surface of the spheroid and to zero at infinity. The constant V_0 will then be determined for the extra condition imposed, *e.g.*, zero potential on the axis, or zero total charge.

Changing to prolate spheroidal coördinates we may write, for the equations of intersecting surfaces,

$$\frac{x^2}{d^2 \operatorname{ctnh}^2 \alpha} + \frac{y^2 + z^2}{d^2 \operatorname{csch}^2 \alpha} = 1 \quad \text{(prolate spheroid)},$$

$$\frac{x^2}{d^2 \tanh^2 \beta} - \frac{y^2 + z^2}{d^2 \operatorname{sech}^2 \beta} = 1 \quad \text{(hyperboloid of revolution)},$$

where $2d$ is the distance between the common foci. α and β are now the coördinates of a point in space. In this system of coördinates Laplace's equation assumes the form,

$$\sinh^2 \alpha \frac{\partial^2 V}{\partial \alpha^2} + \cosh^2 \beta \frac{\partial^2 V}{\partial \beta^2} = 0. \tag{3}$$

α may range from ∞ to 0, β from $-\infty$ to $+\infty$. β is taken negative for points to the left of the plane through the origin perpendicular to the axis of rotation. To transform from rectangular coördinates to the above system we have

$$x = d \operatorname{ctnh} \alpha \tanh \beta \qquad y^2 + z^2 = d \operatorname{csch} \alpha \operatorname{sech} \beta.$$

It is known that the solutions of Laplace's equation as given above, applying to external and internal points respectively, are

$$V_1 = \Sigma A_n P_n(\tanh \beta) P_n(\text{ctnh } \alpha), \tag{4}$$
$$V_2 = \Sigma B_n P_n(\tanh \beta) Q_n(\text{ctnh } \alpha), \tag{5}$$

where P_n and Q_n are the ordinary Legendre coefficients of the first and second kind respectively.

Equation (2) after transformation of coördinates gives for the potential on the surface of the spheroid, $\alpha = \alpha_0$,

$$V = \frac{B\omega}{2c} d^2 \operatorname{csch} \alpha_0 \operatorname{sech} \beta + V_0. \tag{6}$$

This must now be put into the form of (5) for the surface of the spheroid and the coefficients so chosen as to make (5) equal this when α_0 is put for α.

The result is, using

$$P_2(\text{ctnh } \alpha_0) = \tfrac{1}{2}(3 \text{ ctnh}^2 \alpha_0 - 1),$$

$$V = \frac{2B\omega d^2}{9c}\left[\frac{P_2(\text{ctnh } \alpha_0) - 1}{Q_0(\text{ctnh } \alpha_0)} Q_0(\text{ctnh } \alpha) - \frac{P_2(\text{ctnh } \alpha_0) - 1}{Q_2(\text{ctnh } \alpha_0)} P_2(\tanh \beta) Q_2(\text{ctnh } \alpha)\right] + V_0 \frac{Q_0(\text{ctnh } \alpha)}{Q_0(\text{ctnh } \alpha_0)}.$$

This can be simplified since

$$P_2(\text{ctnh } \alpha_0) - 1 = \frac{1}{2}(3\text{ctnh}^2 \alpha_0 - 1) - 1 = \frac{3}{2}\left(\frac{a^2}{d^2} - 1\right) = \frac{3b^2}{2d^2}.$$

$$V = \frac{1}{3}\frac{B\omega b^2}{c}\left[\frac{Q_0(\text{ctnh } \alpha)}{Q_0(\text{ctnh } \alpha_0)} - \frac{P_2(\tanh \beta) Q_2(\text{ctnh } \alpha)}{Q_2(\text{ctnh } \alpha_0)}\right] + V_0 \frac{Q_0(\text{ctnh } \alpha)}{Q_0(\text{ctnh } \alpha_0)}. \tag{7}$$

If the spheroid is insulated, the total quantity of electricity upon it is zero. This means that at an infinite distance from the origin the potential must vanish to a higher order than would be the case if the spheroid contained a resultant charge. Now $d \cdot \text{ctnh } \alpha$ is the major axis of a coordinate spheroid defining a position in space, and is therefore of the same order of magnitude as r, the distance from the origin. Thus, the potential due to the insulated spheroid must vanish to a higher order than $1/\text{ctnh } \alpha$ at infinity.

$$Q_0(\text{ctnh } \alpha) = \frac{1}{2} \log \frac{\text{ctnh } \alpha + 1}{\text{ctnh } \alpha - 1}$$

$$= \frac{1}{\operatorname{ctnh}\alpha} + \frac{1}{3\operatorname{ctnh}^3\alpha} + \frac{1}{5\operatorname{ctnh}^5\alpha} + \cdots.$$

$$Q_2(\operatorname{ctnh}\alpha) = \frac{1}{2}P_2(\operatorname{ctnh}\alpha)\log\frac{\operatorname{ctnh}\alpha + 1}{\operatorname{ctnh}\alpha - 1} - \frac{3}{2}\operatorname{ctnh}\alpha$$

$$= \frac{2}{15}\frac{1}{\operatorname{ctnh}^3\alpha} + \frac{4}{35}\frac{1}{\operatorname{ctnh}^5\alpha} + \cdots.$$

It is seen that $Q_0(\operatorname{ctnh}\alpha)$ contains terms in $1/\operatorname{ctnh}\alpha$ but that $Q_2(\operatorname{ctnh}\alpha)$ contains no such terms. The only way then, in which the potential can vanish at infinity to a higher order than $1/r$ is that the coefficient of $Q_0(\operatorname{ctnh}\alpha)$ for the potential is zero. This determines V_0 as

$$V_0 = -\frac{1}{3}\frac{B\omega b^2}{c}. \tag{8}$$

We have therefore for the potential at an external point due to the insulated spheroid

$$V = -\frac{B\omega b^2}{3c}\frac{P_2(\tanh\beta)}{Q_2(\operatorname{ctnh}\alpha_0)}Q_2(\operatorname{ctnh}\alpha).$$

It is interesting that this potential is independent of the length of the major axis of the spheroid. If the axis is earthed then $V_0 = 0$ and we have from (7),

$$V = \frac{1}{3}\frac{B\omega b^2}{c} - \left[\frac{Q_0(\operatorname{ctnh}\alpha)}{Q_0(\operatorname{ctnh}\alpha_0)} - \frac{P_2(\tanh\beta)Q_2(\operatorname{ctnh}\alpha)}{Q_2(\operatorname{ctnh}\alpha_0)}\right]. \tag{9}$$

The potential at any point on the surface of the insulated spheroid is

$$V = -\frac{1}{3}\frac{B\omega b^2}{c}P_2(\tanh\beta) \tag{10}$$

and that at any point of the spheroid with earthed axis is

$$V = \frac{1}{3}\frac{B\omega b^2}{c}[1 - P_2(\tanh\beta)]. \tag{11}$$

The change of potential due to earthing the axis is therefore

$$\Delta V = \frac{1}{3}\frac{B\omega b^2}{c}.$$

Although our formula has been worked out in Heaviside units these results are also true when V is in ordinary electrostatic units and B is in ordinary electromagnetic units. If the axis remains earthed and B is reversed in sign then the spheroid alters its charge to the extent corre-

sponding to a change of potential of amount

$$\Delta V = \frac{2}{3}\frac{B\omega b^2}{c}. \tag{12}$$

Application to Experiments on the Rotation of Magnetized Bars.—We shall make a rough calculation which will give us the order of magnitude of the effect to be expected in an actual experiment. The case will be that of an iron cylinder rotating in a solenoid and having a cylindrical shell surrounding it inside the solenoid. The shell is connected to an electrometer so that the change in potential on reversing the magnetizing current may be measured. This change will be, making the assumption that the cylinder is the equivalent of a spheroid whose minor axis is equal to the radius of the cylinder,

$$\Delta V = -\frac{2}{3}\frac{B\omega b^2}{c}\frac{q_{12}}{q_{22}} = -\frac{4\pi n B b^2}{3c}\frac{q_{12}}{q_{22}},$$

where n is the number of revolutions per second, b the radius of the cylinder, q_{12} and q_{22} are the ordinary coefficients of induction and capacity, the ellipsoid being the body denoted by subscript unity and the surrounding shell that denoted by subscript 2. Suppose $B = 18{,}000$, $n = 100$, $b = 4$ cm. Let the radius of the cylindrical shell be 4.5 cm. and the lengths 50 cm. Then since the shell completely surrounds the inner cylinder,

$$q_{12} = -q_{11} = -\frac{50}{2\log\frac{4.5}{4}} = -221 \text{ cm. about.}$$

Take $q_{22} = 300$ cm. Substituting these values in (12) we obtain for the change in potential of the cylindrical shell due to the reversal of the magnetizing current in the solenoid, $\Delta V = 0.88$ volt.

Bearing of the Results upon Experiments on Unipolar Induction.—Experiments with the object of detecting the electric field of rotating magnetized bodies have been made by E. H. Kennard[1] and by S. J. Barnett.[2] In these cases the rotating system was surrounded by a shield for the purpose of protecting the electrometer system from accidental electrostatic effects. Presumably the idea was held that, in so far as the magnetic lines existed outside the shell, the latter would have no effect on the phenomena primarily under investigation. While it is true that the ultimate effect is dependent upon an electric field which is of electrostatic origin, and which is consequently rendered impotent as

[1] "Kennard," Phil. Mag., S. 6, 23, 937, 1912.

[2] Barnett, Phys. Rev., (1) xxv, 323, 1912.

regards its influence on the electrometer system on account of the shield this field arises as a direct consequence of the electromagnetic actions under investigation, and is not to be put in the category of accidental or irrelevant disturbances. Had this field been observed in the experiments cited, and had there been no question as to its not being of accidental origin, its experimental realization would undoubtedly have been regarded as a factor of fundamental interest in relation to the phenomena under examination. The comparatively large magnitude of the effect (an increase of 0.88 volt in the electrometer system) which the foregoing calculation shows to be possible provided the effect is not shielded off, is therefore not without interest.

I am grateful to Professor W. F. G. Swann, who suggested the problem, for his interest and advice.

UNIVERSITY OF MINNESOTA, November, 1921.

HALL EFFECT AND SPECIFIC RESISTANCE OF SILVER FILMS.

By G. R. Wait.

Synopsis.

Hall Effect and Specific Resistance of Silver Films, 200 to 20 μμ. Thick.—In agreement with previous results, the specific resistance increased more and more rapidly with decreasing thickness, becoming infinite for about 20 μμ. On the other hand the Hall coefficient was found to be the same in the films as in the bulk metal. The thicknesses were computed from the weight of silver in each film, assuming the density that of the bulk metal. The films were obtained by chemical deposition.

Theory of Electrical Conduction in Thin Films.—After discussing various proposed theories in the light of the above results, it is concluded that these and other facts are in harmony with the simple conception that the film consists of granules, each having the properties of the bulk metal, and that conduction occurs only along strings of granules in contact.

Brashear Method of Depositing Silver Films.—Exceptionally hard films whose resistance, instead of decreasing, increased slightly with time, were obtained by using about four times the amount of sodium hydroxide specified.

Historical.

Miss Stone[1] in 1898 found that the specific resistance of thin silver films was greater than that of bulk metal, and that it increased with decreasing thickness of the film down to a thickness between 50 μμ and 60 μμ, where it almost suddenly became very great. Other workers in the field of films, since that time, have obtained similar results. Among the contributions to this field may be mentioned the work of Vincent,[2] Longden,[3] Patterson,[4] Reide,[5] Swann,[6] Pogany[7], Weber and Oosterhuis,[8] and King.[9]

Moreau[10] made an investigation of the Hall effect in silver and nickel films. He found that the coefficient of the Hall effect in the films was not constant for various thicknesses, being much greater than the value in bulk metal for the smaller thicknesses and decreasing to smaller values than that in bulk metal at a thickness greater than about 60 μμ.

[1] Phys. Rev., (1), vi, p. 1, 1898.
[2] Ann. d. Chim. et Phys., 7, p. 421, 1900.
[3] Phys. Rev., (1), xi, p. 40 and p. 84, 1900.
[4] Phil. Mag., 4, p. 652, 1902.
[5] Ann. d. Physik, 6, p. 881, 1914.
[6] Phil. Mag., 28, p. 467, 1914.
[7] Phys. Zeitsch., 15, p. 563, 1914.
[8] K. Akad. Amsterd. Proc., 19, p. 597, 1917.
[9] Phys. Rev., (2), x, p. 291, 1917.
[10] Journ. de Physique, 10, p. 478, 1901.

EXPERIMENTAL METHODS.

Deposition of Films.—The resistance of films, obtained by the Brashear[1] method of chemical deposition, decreased with time, a phenomenon experienced by other investigators. By increasing to about four times the amount of sodium hydroxide specified in this method, exceptionally hard films were obtained, their resistances increasing slightly with time, occasioned probably by a combination of the film with gases of the air. Cleanliness of the glass surface and purity of chemicals were extremely important in the production of satisfactory films.

Determination of Thickness.—The thickness of a film was determined from the weight of the silver composing it and, as a check, from the weight of silver iodide after the film was transformed. The densities of silver and silver iodide were assumed to be those of bulk silver and ordinary silver iodide respectively. Determinations of thickness by the two methods of weighing were used only after they had been proved superior to the Newton ring method by a rather extensive investigation.

Measurement of Resistance.—The resistance of the films was measured as soon as possible after they were dry, or usually a few minutes after being removed from the solution. In order to determine the contact resistance between the electrode and the film, four electrodes were placed upon the film. Let a, b, c, d represent the four electrodes, c and b being placed very near to each other at one end of the film and a and d near each other at the opposite end; then using the measurements of resistances between a and b, a and c, a and d, b and c, b and d, c and d, six equations were formed from which two independent values of the film's resistance were found.

Measurement of the Hall Effect.—The films were cut into the shape shown in Fig. 1, the electrodes for the primary current being connected at A and B, while those for the measurement of the Hall effect were connected at C and D. The latter electrodes could be shifted accurately by removing some of the film at one or both of the narrow necks. The equipotential points could thus be easily found and permanently retained.

The film under investigation was placed in a holder made of insulating fiber (Fig. 2) upon which had been fastened three electrodes and a groove

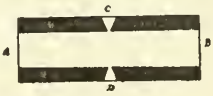

Fig. 1.

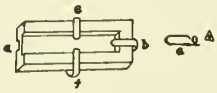

Fig. 2.

for the fourth. The electrodes were made of spring phosphor bronze

[1] Astrophys. Journal I, p. 252, 1898.

and shaped as shown in Fig. 2. In order to secure the best contact between the electrode and the film, the point *o* of the electrode was fitted into a small dent of a triangular piece of copper whose underside had been made plane. This triangular piece of copper was placed upon the film with a small piece of aluminum foil separating the two. The above holder and design of electrodes were used in the measurements of the resistance as well as the Hall effect.

The experimental arrangement for the measurement of the Hall effect consisted of a double potentiometer and is shown in Fig. 3, A, B, C, and D are resistance boxes, the resistances in B and in C being large in comparison with the resistances in A and in D, respectively. The drop across the box D was so adjusted that it was just equal to the Hall effect. G_1 is a Leeds and Northrup galvanometer having a sensitiveness of about 10^{-8} volts per mm. scale deflection. B_2 is a storage cell furnishing the primary current for F. A_1 is an ammeter for the measurement of this current, which was varied (by altering R) from approximately 0.0015 to 0.03 ampere, the thicker films permitting the larger currents.

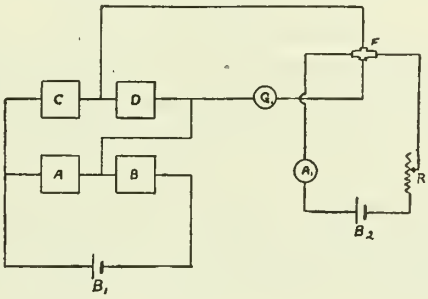

Fig. 3.

Since the Hall effect was measured by taking the drop in potential across D necessary to prevent a deflection of the galvanometer G_1, then $E = \frac{A V \frac{1}{2} (D_1 - D_2)}{(A + B)(C + D)}$, where E is the value of the Hall effect in c.g.s. units, D_1 and D_2 are the values of D necessary to prevent a deflection of G_1 with the magnetic field in opposite directions, A, B and C are the resistances shown and V s the potential difference of the cell B_1, measured in c.g.s. units.

The magnetic field was furnished by a large electro-magnet, the faces of whose pole pieces were four centimeters in diameter and one centimeter apart. The field strength was measured by means of a bismuth spiral calibrated for this purpose. The measurement of the field for different currents through the magnet over a duration of five years using

two different spirals gave differences of only 0.8 per cent. The fields used were from 5,000 to 12,000 lines per cm.^{2}

TABLE I.

Film	ε.	E/HI.	R	Residuals.	Film	ε.	E/HI.	R	Residuals.
42	21	320	805	30	9	40	216	20.7	19
34	21	...	3 x 10″	..	33	43	164	3.5	2
28	22	...	3 x 10″	..	37	46	188	8.3	..
36	23	321	200	..	27	47	118	3.9	6
41	28	325	9.7	3	31	50	138	3.8	4
33	29	314	10.8	9	7	51	143	12	11
35	31	284	5.8	17	4	51	170	8.8	7
23	33	295	8.5	6	30	54	185	5	11
32	36	232	8.6	2	40	89	108	2.8	2
18	38	182	10	13	29	109	74	3.7	5
26	38	202	9.4	18	10	182	47	2.6	7
43	40	212	9.3	8					

EXPERIMENTAL RESULTS.

In Table I. are given the results of the present investigation. In column one is given the film number; in column two, its thickness in millimicrons, the mean of the thickness obtained upon the basis of the weight of the silver and its weight after it had been transformed into silver iodide. The third column gives E, the Hall e.m.f. divided by the product of the magnetic field H, in e.m.u. and the primary current I in c.g.s.u. In most instances four different strengths of the magnetic field were used, in which case there were four values for E/HI; the one given in column three is the mean of the four. The mean residual for each film is recorded in column five. A particular residual was obtained by taking the differences between the mean E/HI and the E/HI for that particular field and current. Column four contains the resistance in 10^{-6} ohms per cm.^{3} of each film. For two films the Hall effect is not given, this being due to the fact that it was not possible to obtain measurements of the effect for films having such high resistances. Although considerable data have been obtained by various investigators upon the variation of specific resistance of films with their thickness, and also som data upon coefficients of the Hall effect, the author, is not aware that the two phenomena have ever been studied for the same film. It is important, if results upon the two phenomena be used in conjunction with each other, that they be obtained from the same film. This would be even more important for films that change with time.

Specific Resistance.—In Fig. 4 is plotted ρ, the specific resistance, against

ϵ, the thickness of the films. It will be seen that for films having the greater thickness the ρ is very little greater than its value in bulk silver, and seems to approach asymptotically to that value. The value of ρ gradually increases toward decreasing thickness until about 50 $\mu\mu$ is reached, when it increases much more rapidly. It will be seen that the value of ρ seems to approach ∞ in the neigh- borhood of 20 $\mu\mu$.

Hall Effect.—As is well known, the Hall e.m.f., E, is given by the rela-

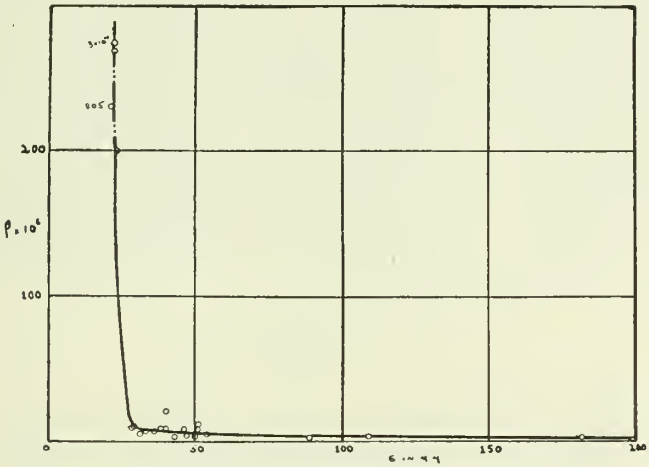

Fig. 4.

tion $E = (HI/\epsilon)\alpha$ wherein α is the Hall coefficient. In numerous tests with silver films herein described, E was found to be proportional to H and I. The values of E/HI for various values of ϵ, given in Table I., are

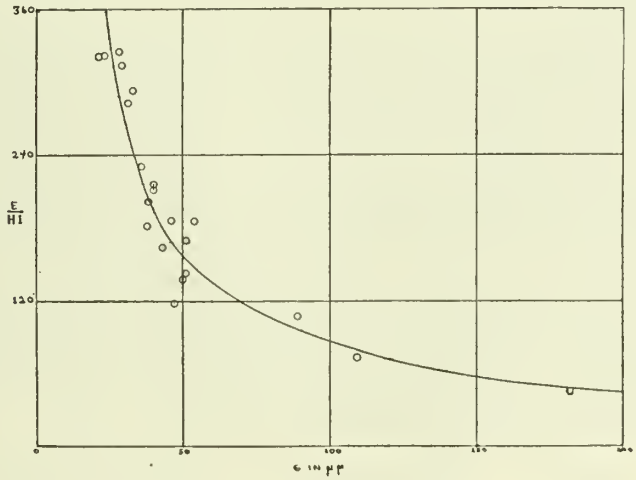

Fig. 5.

plotted in Fig. 5 in which is drawn a hyperbola with $\alpha = 0.00084$, the accepted value of the Hall coefficient in silver. It will be seen that the curve fairly represents their mean. Thus the value of α, the Hall coefficient, in the films is the same as in bulk silver and is constant for all thicknesses investigated greater than 23 $\mu\mu$.

Theoretical Considerations.

Assuming that there is a diffusion of negative electrons through the spaces between the atoms, that the electrical properties of the metal arise entirely in the average motion impressed by external circumstances on the swarm of electrons which are otherwise moving about quite freely in the spaces between the atoms, and that the distribution of velocities among them at any instant is precisely that specified by Maxwell's law, the electron theory of the Hall effect leads to the following well-known result for the electric field in the z-direction at right angles to the direction of current density in the y-direction J_y, and to the magnetic field of intensity H in the x-direction:

$$E_z = -\frac{3\pi}{8\,Nec} HJ_y.$$

E_z is the electric field of uniform intensity produced in the z-direction, the current density, J_z, being supposed zero; N is the number of free electrons per unit volume, e the charge on the electron, and c the ratio of units. This result is in accord with experiments in a large number of cases. Without further assumptions it is not possible to apply the result of the theoretical investigation to a thin film wherein the material is supposed to consist of granules not in the intimate contact obtaining in bulk form.

Let us assume that J_y' is constant through the xz cross-section of any granule and that the packing of granules is sufficiently close to warrant the approximate statement that the current through the film cross-section is carried by the granules and not by gaps. Consider the xz cross-section. We are concerned with a gross result rather than what occurs in the individual granule, and consequently we are induced to idealize the location of these granules in order to simplify our own thinking. Let us assume that we have a layer of similar granules of thickness Δx. All of them may not be carrying current and in those that do, the current densities are not the same. The total difference of potential across this film will be $\Sigma E_z' \cdot \Delta z$ where Δz is the approximate width of the granules, and $\Delta x.\Delta z$ is the area of the granule in cross-section. But,

$$\Sigma E_z'\Delta z = -\frac{3\pi}{8\,Nec} \mathrm{H}\Sigma J_y'\Delta z = -\frac{3\pi}{8\,Nec} H\Sigma J_y' \frac{\Delta x \cdot \Delta z}{\Delta x}$$

or

$$E = -\frac{3\pi}{8\,Nec} HJ,$$

where J is the current per unit thickness.

In the expression for E_z, the value of current density J_y was introduced by assuming that in the granule $J_y = \sigma E_y$, where σ is the conductivity determined by the same assumptions as to electrons, and E_z is the electric field. In applying this theory to the granule, we have thus assumed consistently that the theory applies to the granules the same as to the bulk metal. Our conclusion is that the coefficient should be constant irrespective of the specific resistance or thickness of the film, and that it should be the same as in bulk metal. Both of these points are verified by experiment as already shown. The assumptions seem therefore to be in agreement with the experimental facts, and the author will assume the correctness of this simple theory of thin films, namely that they are composed of granules having the property of bulk metal and of conducting gaps which give resistance only.

J. J. Thomson[1] explained the variation of specific resistance of films with thickness by assuming that the mean free path of the conducting electron was less in the film than in the bulk metal. The curve drawn based upon such an assumption, however, is not so steep as the experimental curve. Patterson suggests that this may be due to a gradation in the density of electrons from the inner part of the film toward the outer boundaries. Swann[2] assumed that the mean free path of the conducting electron varied with temperature the same in the film as it does in bulk metal. By measuring the specific resistance of platinum films over a wide range of temperature he obtained results which show that Thomson's explanation is not in agreement with experimental facts. The present investigation furnishes direct information regarding Patterson's suggestion pertaining to the change in the number of conducting electrons per unit volume. From Patterson's assumptions alone, the thinner films should show the greater value for the coefficient and its value should approach that in bulk metal as the thickness is increased. Instead of this, however, the Hall coefficient is always constant, having the same value as in bulk metal.

Moreau[3] explained his results for the Hall effect in films by means of Vincent's transition layer theory. The results of the present investigation, however, are not in accord with Moreau's results nor with Vincent's theory. Now Vincent was able to explain the rapid increase in specific

[1] Phil. Mag. (4), p. 675, 1902.

[2] Loc. cit.

[3] Phil. Mag. (4), p. 675, 1902.

resistance upon the assumption that the specific resistance of the film of metal between the transition layers was that of ordinary metal, while the resistance of the layers was constant and quite great. Obviously, the Hall coefficient, which depends upon the number of conducting electrons per cm.^{3} would therefore change at the thicknesses where the increase in specific resistance is so marked. No such change was detected experimentally.

Swann,[1] found the three following interesting facts: (*a*) Thick films underwent an increase in resistance with increase in temperature, (*b*) thin films underwent a decrease in resistance with increase in temperature, and (*c*) films having a thickness between these had an apparent zero temperature coefficient of resistance over most of its range. Now, the change in a film's resistance, when its temperature is increased slightly, will depend at least upon the three following factors: (1) Expansion of the glass, upon which the film is deposited. (2) Expansion of metal composing the groups bringing them into more intimate contact. (3) The regular temperature coefficient of the metal. For very thin films the effect of (2) will be to decrease the resistance, as the temperature is increased; for thicker films this effect may be very small as may be seen from the following considerations. In the case of very thin films it was seen that a very small addition of groups produced a great decrease in the resistance, but that the addition of the same number of groups to a thick film decreased the resistance very much less. Similarly an expansion of groups might be expected to produce a great change of resistance in the case of thin films, and a small change in the case of the thicker ones. The above considerations make possible an explanation of the so-called temperature coefficients, and permits the simple assumption that the addition of groups have the effect of decreasing the number of conducting paths through the film, by combining many that are already present and making them straighter and wider.

The general conclusion is that the experiments herein recorded and all others in thin films are in harmony with the simple theory here proposed, namely that we are dealing with granules which have the same electrical properties as bulk metal and with conducting gaps.

The author wishes to express his appreciation to the Physics Department of the State University of Iowa for valuable assistance received, and especially to Professor G. W. Stewart under whose direction this work was carried on, and whose encouragement and criticisms made the work possible.

PHYSICAL LABORATORY, STATE UNIVERSITY OF IOWA.

[1] Phil. Mag. (4), p. 675, 1902.

THERMAL ANALYSIS AT LOW TEMPERATURES.[1]

By Frank E. E. Germann.

Synopsis.

Cooling and Heating Curves for Water Solutions of Uranyl Nitrate between 0° and −70° C.—A thermo-junction was placed in 0.5 cc. of a solution of known concentration and galvanometer readings were taken every 10 seconds during the cooling. At about −35° a rapid evolution of heat took place accompanied by expansion sufficient to break the glass tube if the solution filled more than the rounded bottom. On heating the solution a corresponding absorption of heat was observed at −20°. From the observed temperature changes and the specific heat the amount of heat evolved or absorbed was computed. The results of 67 experiments in which the *concentration was varied from 10 to 55 per cent.* were plotted and show a sharp maximum at 48.0 per cent. for the evolved heat and at 47.5 per cent. for the absorbed heat.

New Compound Discovered by Thermal Analysis, Uranyl Nitrate Icositetrahydrate.—The above results point to the formation at −35° of the compound $UO_2(NO_3)_2.24H_2O$, which has a less density than the hexahydrate and which decomposes spontaneously at −20°. This compound is of special interest in connection with the study of the relation between composition and the fluorescence and absorption of the spectra uranyl hydrates.

THE study of chemistry and chemical reactions is usually restricted to those compounds which are stable or in a state of false equilibrium at room temperatures. As a result, many compounds which might be stable at very high or very low temperatures are never discovered. The present article serves to illustrate how such compounds may be studied by means of cooling and heating curves. The cooling curve might be regarded as a method of determining the composition by synthesis, whereas the heating curve might be regarded as a method of analysis.

When a water solution of uranyl nitrate is cooled to the temperature of liquid air, it is possible to get various distinct fluorescence spectra from it, depending in general on the rate of cooling. H. L. Howes[2] has described what seemed to him to be five distinct spectra, varying from a sharp-line spectrum in the case of slow cooling to a broad-banded spectrum in the event that the solution was plunged directly into liquid air. The other spectra were the results of other chance intermediate methods. As far as we know today, the emission and absorption spectra

[1] Paper presented to American Physical Society (see abstract in Phys. Rev., 11, p. 245, 1918).

[2] Phys. Rev. (2), Vol. VI., p. 192, 1915.

of elements and compounds are very characteristic at any given temperature, so that it would seem quite impossible to obtain more than one fluorescence spectrum for a given compound. The only logical explanation that the author could advance for the anomaly observed by Mr. Howes was that the uranyl nitrate formed one or more definite hydrates at low temperatures, the transformation taking place entirely in the solid phase. Professor Edward L. Nichols drew the author's attention to the work of Mr. Howes, and the research here discussed was carried out in order to prove or disprove the above conclusion.

Temperatures were measured by means of a copper-advance thermojunction in series with a resistance of about nine thousand ohms and a sensitive d'Arsonval galvanometer. The filament of a Nernst lamp was focused on a wall opposite the galvanometer at a distance of about five meters. The maximum deflection read was of the order of one meter, so that a linear relation between deflection, voltage, and temperature could be assumed. Accordingly deflections are used constantly in what follows, without any transformation to temperatures except in the final results of range of stability. One junction was kept packed in ice, while the other was placed directly in the specimen under examination while still in a liquid state.

Preliminary tests showed that if water solutions of uranyl nitrate were cooled in a carbon-dioxide-ether mixture, the tube was usually broken. The heavier the walls and the smaller the bore of the tube, the more completely was the container shattered. Using a thick walled capillary tube was found to prevent the breaking. However, when a thermojunction was placed in the solution in a tube that would break, a sudden rise in temperature was indicated by the galvanometer at the same instant that the tube gave way. In the case of a strong capillary tube no such rise was noted. Inasmuch as it would be valuable to heat and cool the same specimen frequently, as well as to use the same tube for specimens of different concentrations, it was necessary to permit the expansion as well as to prevent the breaking of the tube. To accomplish this, a test tube of such a diameter was used that one half cubic centimeter of solution would all be contained in the lower hemispherical volume. Thus the expansion could all take place upwards, and the same tube could be used for all experiments. Since the fused end of the thermojunction was no larger than a pin head, the small volume offered no difficulty.

A constant temperature gradient was obtained by placing the tube containing the specimen in two larger concentric test tubes which were all separated by cork rings and cotton. This gave two air chambers between the inner tube and the carbon-dioxide-ether mixture.

The best obtainable C.P. uranyl nitrate was recrystallized as the hexahydrate, and water solutions varying from ten to sixty per cent. by weight anhydrous salt were prepared and preserved in glass-stoppered bottles. An accurately calibrated half cubic centimeter pipette was used to measure out the samples to be tested. Since we are measuring the amount of chemical reaction by means of the quantity of heat liberated, we should always deal with the same total number of mols or molecules of water and uranyl nitrate. It is more simple, however, to deal with the same volume of the various solutions. We are justified in doing this since the result is the same in either case. In this particular case the curve may be different but the maximum will be the same. The heat liberated in any case would be the continuous product of the specific heat c, the mass m and the change in temperature t. The quantity of heat with which we would be concerned would be this product divided by the total number of mols of water and salt M, or heat per mol solution $= cmt/M$.

Plotting values of t as ordinates and values of percentage as abscissæ, we obtain a curve showing a sharp maximum. The values of c and M decrease while m increases with increasing concentration. The value of cm/M is almost constant. The product of the ordinates of a curve showing a maximum by values differing only slightly from a constant gives a curve whose maximum has the same value of the abscissa as the original curve. Accordingly we are justified in this particular case in plotting values of t against per cent. of $UO_2(NO_3)_2$.

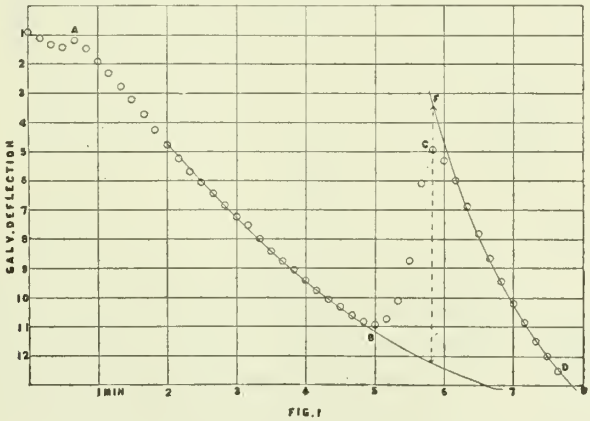

Fig. 1.

Referring to Fig. 1 we can get an idea of the appearance of the various cooling curves. At A the solidification of uranyl nitrate as hexahydrate and ice is complete, and we have the heterogeneous solid cooling uni-

formly to B. At this point a rapid evolution of heat takes place simultaneously with the expansion previously mentioned, bringing the temperature back up to C. Here the cooling again begins, and we finally arrive along a smooth cooling curve at D. Galvanometer deflections were read every ten seconds. By extrapolating the curves AB and CD, and drawing the line EF vertically through C, we obtain a length EF which is proportional to the heat liberated and consequently proportional to the chemical reaction. Similar curves were run for 20, 30, 45, 46.47, 47.75, 48, 49, 50, 52, and 55 per cent. The number of determinations for each percentage varied from two to ten. It is obvious that zero per cent., representing pure water, would give a zero value of t, and would be a point on the curve. Similarly there could be no rise in temperature if we use a concentration such as we have in the pure hexahydrate, which is the normal hydrate at ordinary temperatures. The compound $UO_2(NO_3)_2.6H_2O$ contains 78.48 per cent., by weight of uranyl nitrate and accordingly this value with $t = 0$ would also be a point on the curve.

Fig. 2 is the weighted least square curve of all the observations. The

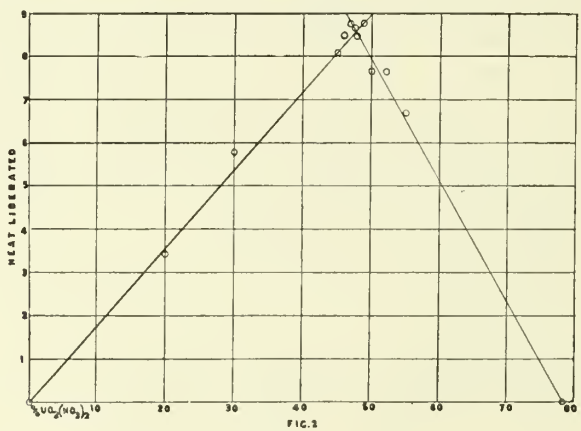

Fig. 2.

curve represents the results of forty-nine experiments. No values were discarded. The two lines, which are sensibly straight, intersect at 48.00. Multiplying all the ordinates of these lines by the respective values of cm/M, which remain practically constant, would give a curvature to the lines, but, as shown before, the abscissa of the maximum would remain the same.

If we now take a specimen which had been transformed, and allow it to warm up slowly with a definite temperature gradient, and take readings of the galvanometer as before, we obtain a curve of the type of Fig. 3. In this case the amount of chemical transformation would be evidenced

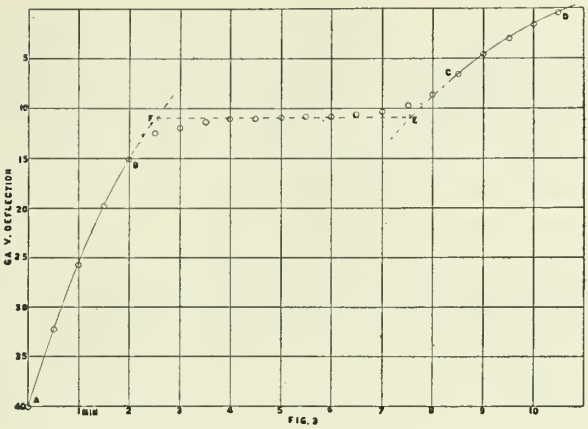

Fig. 3.

by a length of time *FE* of constant temperature. Here again galvanometer readings were taken every ten seconds. The points 0 and 78.48 may again be used with $t = 0$, together with the six other points determined experimentally. Each of these points is the average of three

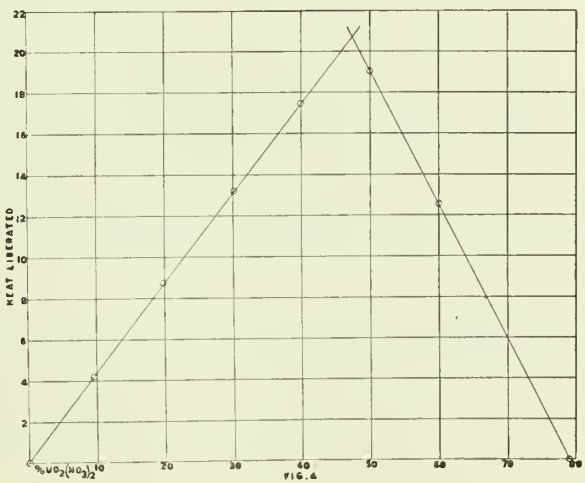

Fig. 4.

determinations. Hence Fig. 4 represents a total of eighteen experiments. As will be seen from the curve, the points fall almost exactly on the two straight lines, which intersect at 47.50. The experiments involved in the formation of Fig. 2 were not as accurate, as the methods of procedure had not been well worked out. It would seem logical, therefore, to assign equal weights to the two curves. The probable error would be $\pm$ 0.17, so that the composition of the hydrate formed would

be 47.75 ± 0.17 per cent. A hydrate containing twenty-four molecules of water would consist of 47.69 per cent. uranyl nitrate, which falls within the limits mentioned. Twenty-three and twenty-five molecules of water would be equivalent to 48.70 per cent. and 46.70 per cent. uranyl nitrate respectively. We are therefore led to the conclusion that a hydrate exists whose composition given by 47.75 ± 0.17 per cent. uranyl nitrate, and whose formula is $UO_2(NO_3)_2.24H_2O$. The name of the compound would be uranyl nitrate icositetrahydrate.

Since the incositetrahydrate forms spontaneously while in the presence of the hexahydrate, it is probable that it also crystallizes in the rhombic system, which is the system of the hexahydrate. Due to the low temperatures involved, it was impossible to determine this with ease, so that phase of the work was not followed up. It is also probable that another hydrate of some other crystalline system exists between the hexahydrate and the icositetrahydrate, but which was not observed because of the absence of seed crystals of the correct form.

The icositetrahydrate forms spontaneously at about − 35° C. and decomposes at about −20° C. It could consequently never be studied at ordinary temperatures and pressures. The cooling curves were actually studied down to about − 70° C. The explanation of the anomolies observed by Mr. Howes are now obvious. Slow cooling of a 47 to 48 per cent. solution of uranyl nitrate would give almost a pure-line spectrum of the icositetrahydrate. Rapid cooling of the same might give a spectrum of the hexahydrate in the case of a complete suppression of the transformation, and a mixed spectrum in the case of a partial transformation. It is obvious that many possibilities are offered by different concentrations, and it is not strange that at least five fairly distinct types were picked out as actually existing.

The discovery of this new compound is of more than passing interest, since it adds another member to a series of hydrates studied by Nichols and Merritt in a paper entitled "The Influence of Water of Crystallization upon the Fluorescence and Absorption Spectra of Uranyl Nitrate."[1]

The above research work was done in the laboratories of the Department of Physics of Cornell University while the author was a Carnegie Research Associate. The author wishes to express his gratitude to Professor Nichols for suggesting the problem and to Professor Hutchinson of the Department of Engineering Mathematics of the University of Colorado for valuable suggestions in connection with the curves.

DEPARTMENT OF PHYSICAL CHEMISTRY,
UNIVERSITY OF COLORADO,
BOULDER, COLORADO,
December 6, 1921.

[1] PHYSICAL REVIEW (2), Vol. IX., pp. 113–126, 1917.

THE UNILATERAL DYNAMIC CHARACTERISTICS OF THREE-ELECTRODE VACUUM TUBES.[1]

By John G. Frayne.

Synopsis.

Unilateral dynamic characteristics of vacuum tube when plate circuit includes resistance, inductance or capacity.—(1) *Theoretical equations.* For the case of pure resistance (R), the Van der Bijl parabolic relation between plate current and effective grid voltage is expressed as a power series in $e \sin pt$, the impressed simple harmonic grid voltage. The *coefficients of the various harmonics* involve R, the nth harmonic reaching a maximum value when R equals $(n-2)/3$ times R_0 the tube resistance. For the fundamental the *maximum energy output* for a given plate battery is secured when $R = 0.81\ R_0$. The dynamic characteristic was obtained by compounding the harmonics into a single curve; it approaches a straight line as the resistance is increased. For the case of pure inductance, the plate current is expressed as a Fourier series. The dynamic characteristic is a closed loop whose area is proportional to the energy in the inductance. This loop reduces to an ellipse for small values of e, in which case the tube functions as an alternator whose internal impedance is a function of the external load. The insertion of a condenser instead of an equivalent inductance gives identical results except that the phase angle of the various harmonics is shifted. (2) *Experimental verification.* The effects on the plate current of varying the alternating grid voltage e, the static grid voltage E_c and the plate voltage E_b, for a given value of resistance R or inductance l, and the effect of varying R or l with constant E_b, E_c and e (15 or 20 volts), were determined and are shown in curves together with the corresponding theoretical values. A. W. E. 205B tube was used. The results show that the equations predict the harmonic constituents of the plate current as high as the fourth, for values of e up to 15 or 20 volts (depending on E_b), the range for which the fundamental equation holds. For this range the coefficients of the various harmonics in the equation are proportional simply to e^n. The fundamental becomes greater while the other harmonics diminish as we approach the straight portion of the static characteristic and as we increase the plate potential.

Circuit for producing pure sine wave electromotive force with frequency of 200,000 cycles.—The oscillating circuit and filters used are shown diagrammatically in Fig. 1.

Pure resistance for high frequencies.—*A platinized quartz fiber* (diameter 0.01 mm.) with a resistance of 100 ohms per inch will carry 0.06 ampere when immersed in acid-free paraffin oil and has a negligible skin effect.

It is a well-known fact that the current flowing from a hot filament to the plate of a three-electrode vacuum tube does not vary as the first power of the plate potential. With a view to determining what this relation really was, theoretical and experimental investigations were undertaken by Langmuir,[2] Bethenod,[3] Vallauri,[4] Van der Bijl,[5] Latour[6]

[1] Presented at the Chicago meeting of the American Physical Society, December, 1920.

[2] P. I. R. E., 3, 261–93, Sept., 1915, and Phys. Rev., 2, p. 457, 1913.

[3] La. Lum. El., 35, 25–31, Oct. 14, 1916.

[4] L'Elettrotecnica, Vol. 4, Nos. 3, 4, 18 and 19, 1917.

[5] Phys. Rev., 11, p. 172–198, 1918.

[6] La Lum. El., Dec. 30, 1916.

and others. The second degree equation obtained by Van der Bijl lends itself more easily to mathematical treatment than any of the others, and agrees very closely with experimental evidence over a certain range of plate and grid potentials.

The curves obtained by plotting the plate current against the grid voltage for given plate potentials are usually referred to as the static characteristics of the tube. The term "dynamic characteristic" is used when the grid potential is of an oscillating nature. The latter characteristic is usually referred to as being "unilateral" when there is no external coupling between the grid and plate circuits, as distinguished from "regenerative" when such coupling exists. Van der Bijl has shown that the insertion of a resistance between the plate and the plate battery changes the form of the dynamic characteristic from a parabola to a curve which approaches a straight line with increasing resistance. A solution similar to that of Van der Bijl is obtained here, and in addition the case where the resistance is replaced by an inductance is worked out. We shall consider three cases here. First, with no resistance in the plate circuit, secondly, with a resistance inserted, and finally with the latter replaced by an inductance.

Case of No External Resistance.

Let E_b = plate potential,
I_b = plate current,
E_c = grid potential,

$e \sin pt$ = superimposed e.m.f. on grid.

According to the current-squared law

$$I_b = A(E_b + \mu E_c + \mu e \sin pt + \epsilon)^2, \tag{1}$$

where μ is the amplification constant, defined by

$$\frac{1}{\mu} = -\left(\frac{dE_c}{dE_b}\right)_{I_b}$$

and A and ϵ are constants depending on the structure of the tube. In this case the grid potential has the value $E_c + e \sin pt$. The equivalent plate potential is therefore $\mu\ (E_c + e \sin pt)$.

Before proceeding further it might be well to remark here that in order that (1) may actually represent the true conditions the value of e must lie within certain limits, namely

$$e \leqq |E_c| + |g|, \quad e \leqq \left|\frac{E_b + \epsilon}{\mu}\right| - \left|E_c\right|,$$

where g is the maximum positive voltage the grid can have before it

begins to attract many electrons. Also if $e \sin pt$ attains such a large negative value in the cycle that the expression above is negative, the resulting current wave will be flattened out at that part of the characteristic curve. Equation (1) might be written generally as:

$$I_b = f(\mu e \sin pt).$$

Expanding by Maclaurin's Theorem

$$I_b = f(0) + \mu e \sin pt\, f'(0) + \frac{\mu^2 e^2 \sin^2 pt}{2!} f''(0)$$

and since I_b is the same function of E_b as it is of $\sin pt$

$$f'(0) = \left(\frac{d\, I_b}{d\, E_b}\right)_{t=0} = 2\, A\, (E_b + \mu\, E_c + \epsilon) = \frac{1}{R_0},$$

$$f''(0) = \left(\frac{d^2\, I_b}{d\, E_b^2}\right)_{t=0} = 2\, A.$$

Therefore

$$I_b = A\, (E_b + \mu\, E_c + \epsilon)^2 + \frac{\mu e \sin pt}{R} - \frac{A \mu^2 e^2}{2} \cos 2\, pt + \frac{A \mu^2 e^2}{2}. \quad (2a)$$

Thus in the simple case illustrated above where the plate potential is kept constant throughout the operation, a pure sine wave on the grid gives rise to a current of the same frequency (called the fundamental) in the plate circuit, a first harmonic and a rectified current component. In this case the actual dynamic and static characteristic curves will coincide.

Case of a Pure Resistance.

Next we shall consider the case where the potentials on the grid and plate vary simultaneously. Let a resistance R be connected between the plate and the plate battery. Then

$$I_b = A\, \{E - R\, I_b + \mu\, (E_c + e \sin pt) + \epsilon\}^2. \quad (3)$$

This can be expanded as an infinite series.

$$I_b = f(0) + f'(0)\, \mu e \sin pt + \frac{f''(0)}{2!}$$

$$(\mu e \sin pt)^2 + \cdots \frac{f^n(0)}{n!} (\mu e \sin pt)^n \quad (4)$$

Van der Bijl has shown that since the parabolic relation connecting plate current and grid and plate potentials is only an empirical approximation, it is not to be expected that the higher derivatives in the series will accurately represent the actual experimental values. However, the

derivatives up to probably the third or fourth ought to be a close approximation and the higher derivatives ought to indicate, at least in a qualitative way, how the higher harmonics depend on the various tube constants and on the properties of the external circuits.

Referring back to equation (4), the coefficients of the series are as follows:

$$f(0) = \frac{1}{2AR^2}\left\{\frac{1}{2}(B+1) - B^{1/2}\right\}, \quad B = 1 + \frac{2R}{R_0},$$

where

R_0 being defined as $\dfrac{1}{2A(E + \mu E_c + \epsilon)}$,

$$f'(0) = \frac{1}{R}\left\{1 - B^{-1/2}\right\}, \quad f''(0) = A B^{-3/2}, \quad f'''(0) = -2A^2 R B^{-5/2}.$$

The general functional term is given by

$$f^n(0) = \frac{(-1)^n 2^{n-1} n(n-2)(n-4) - \cdots - R^{n-2}A^{n-1}}{n!B^{(2n-1)/2}}.$$

$$= \frac{(-1)^n 2^{n/2-1} R^{n-2} A^{n-1}}{\Gamma_{(n+1)/2}\, B^{(2n-1)/2}}$$

The coefficient of sin (pt) is therefore the value of this expression multiplied by $(\mu e)^n$. If this coefficient is denoted by α_n, then

$$\left|\frac{\alpha_n + 1}{\alpha_n}\right| = \frac{2(n+2)RA\mu e}{(n+1)B},$$

$$\underset{n=\infty}{\text{Limit}} \left|\frac{\alpha_n + 1}{\alpha_n}\right| = \frac{2RA\mu e}{B}.$$

In order that the series (4) may be absolutely convergent

$$\frac{2RA\mu e}{B} < 1.$$

Therefore

$$e < \frac{B}{2RA\mu}, \qquad i.e., < \frac{1}{2A\mu}\left\{\frac{R + 2R}{2RR_0}\right\}.$$

Thus for a given A, μ and R, the smaller the value of R_0, the greater e may be.

Using the values of A, μ, R and R_0 given later, e may have values reaching up to 150 volts. However, it will be seen later that in practice e cannot have a value larger than about 15 volts if equation (3) is to represent conditions accurately. The physical limitations which the tube imposes on the characteristic equation make it impossible to use

grid voltages more than one tenth of the limiting value as given by (5). It is very evident that for small values of e, the series (4) converges rapidly and in consequence only a few terms need be evaluated in order to find a close approximation to the actual current flowing under a certain condition of the amplifier.

Now $f'(O)$ stands for the reciprocal of the total output resistance R'_0 when there is an external resistance in the plate circuit.

Therefore

$$\frac{1}{R'_0} = \frac{1}{R}\left\{1 - B^{-1/2}\right\}$$

The total resistance of the complete plate circuit is thus a rather complicated function of the external resistance and the internal output resistance of the tube when there was no resistance in the plate circuit.

Since the series (4) is a power series in sin (pt) it is necessary to convert the various powers of sin (pt) into first-power expressions of functions of multiples of pt, and expressions corresponding to the rectified currents. Since the series converges rapidly for values of input voltage within the limits (2), all powers of sin (pt) beyond the fourth will be omitted.

$$\begin{aligned} I_b = {} & \frac{1}{2AR^2}\left\{\frac{1}{2}(B+1) - B^{1/2}\right\} \\ & + \left[\left\{\frac{\mu e}{R}(1 - B^{-1/2})\right\} - \frac{3}{2}A^2R\,\mu^3\,e^3\,B^{-5/2}\right]\sin(pt) \\ & - \left[\frac{1}{2}A\,\mu^2e^2\,B^{-3/2} + \frac{5}{2}A^3R^2\mu^4e^4\,B^{-7/2}\right]\cos(2\,pt + \pi) \\ & + \frac{1}{2}\left[A^2\,R\,\mu^3\,e^3\,B^{-5/2}\right]\sin 3\,pt \\ & + \frac{5}{8}\left[A^3\,R^2\,\mu^4\,e^4\,B^{-7/2}\right]\cos 4\,pt + \cdots\cdots\cdots\cdots \end{aligned}$$

Actual computation of the coefficients in this series show that for values of e within the limits specified above, the series converges very rapidly.

For values of e below 10 volts, actual computations show that the coefficient of sin (pt) is practically a linear function of e; beyond ten volts the term involving e becomes appreciable and the relation becomes more complex. Similarly the coefficient of cos $(2\,pt + \pi)$ varies as the square of e up to about 10 volts. Since we have taken no powers higher than sin pt the coefficients of the third and fourth harmonics vary directly as the cube and fourth powers respectively of e.

The relation between the coefficients and R, when the latter is variable, can best be shown by examining the condition for maxima. If we take

the nth derivative as representing the coefficient of the general term, then the latter will be a maximum when

$$\frac{d}{dR}\left(f^n(0)\right) = 0,$$

i.e., when

$$R = \frac{n-2}{3} R_0 \quad \text{or} \quad (1 + 2\,R/R_0)^{-1} = 0.$$

The latter equation has a solution, $R = \infty$. This is, obviously, the condition for a minimum. The first relation shows that R must be a negative quantity for $n = 1$. Hence the fundamental has no real maximum. For $n = 2$, the maximum occurs at $R = 0$. For $n = 3$, the maximum occurs when the external resistance is one third of the tube resistance. For the higher derivatives, the position of the maxima occur at continuously increasing values of R.

If the amplitude of the impressed e.m.f. is less than 15 volts, equation (3) holds good for all values of R, when the plate voltage is maintained at 200 volts, and the grid voltage is -7.5. For values of e over 15 volts, using the same grid and the plate potentials, equation (3) no longer holds. Hence the amplitudes of the harmonics as experimentally found for values of e over 15 volts depend on other features of the amplifier. Since E_c is -7.5 the grid will be raised to a positive potential of 7.5 volts during this cycle. In Fig. 5 it will be noticed that at this value of E_c on the 200-volt parameter, the static characteristic begins to lose its parabolic nature and tends to flatten out. From the nature of the static characteristic it may be seen that the higher the plate voltage is raised the greater the values e may have and remain within the proper limits. This amounts to saying that the smaller R_0 is, the greater the input voltage on the grid may be.

The dynamic characteristics for this case may be obtained as follows: The instantaneous values of the various harmonics for values of pt between 0 and 2π are plotted, and then these constituent sine waves compounded to give the actual wave shape. If now the resulting periodic current is plotted along the I_b axis and the input voltage plotted on the E_c axis, the resulting curve will be the so-called dynamic characteristic of the tube under the specific conditions. It will be seen that if all terms but the fundamental had been neglected, the characteristic would have been a straight line. Addition, however, of the first harmonic causes the characteristic to have a definite curvature. The smaller the value of the external resistance, the more nearly does the curve approach the parabolic relation holding in the static case, and, of course, in the limiting case when R is zero, the two characteristics coincide.

Condition for Maximum Output.

In connection with the expression for the internal resistance, it may be pointed out that the usual statement that the maximum power is obtained from a tube when the external resistance in the plate circuit is equal to the internal output resistance of the tube needs clarification. If by maximum power is meant the greatest power obtained from the fundamental frequency, the following is valid.

$$\text{Power} = R\,I^2 = \frac{\mu^2 e^2}{R}\left[1 - B^{-1/2}\right]^2. \tag{6}$$

Therefore

$$\frac{dP}{dR} = -\frac{\mu^2 e^2}{R}\left[1 - B^{-1/2}\right]\left[\frac{1}{R}\left(1 - B^{-1/2}\right) - \frac{2}{R}B^{-3/2}\right], \tag{7}$$

$$\frac{dP}{dR} = O \text{ for maximum } P.$$

Therefore

$$B^{3/2} = 2B - 1 \quad \text{or} \quad \frac{R}{R_0} = \frac{1 \pm \sqrt{5}}{4} = 0.81. \tag{8}$$

The condition for a maximum dissipation of fundamental current energy is that the ratio of R to the internal resistance when R was zero is .81. This condition holds in the case where the maximum power is desired with a certain fixed-plate battery, and a variable resistance is available. The usual condition for maximum power, that the internal and external resistances be equal, is only true in this case if the actual plate potential is kept constant while the plate resistance is varied. The condition under which the above relation was obtained is the one most commonly met with in practice.

Case of an Inductance.

When an inductance, l, is placed between the plate and plate battery, the equation for the plate current may be written as follows:

$$I = A\left\{E_b - l\frac{dI}{dt} + \mu\left(E_c + e\cos pt\right) + \epsilon\right\}^2 \quad \text{or} \tag{9}$$

$$B^2 - 2BL\frac{dI}{dt} - 2LF\cos pt\frac{dI}{dt} + 2BF\cos pt + L^2\left(\frac{dI}{dt}\right)^2 + F^2\cos^2 pt$$

where

$$B = A^{1/2}\left(E_b + \mu E_c + \epsilon\right). \quad L = A^{1/2}, \quad F = A^{1/2}\mu e. \tag{10}$$

A rigorous solution of this differential equation for I is very difficult. but an approximate method of solving it may be legitimately utilized. Experimental evidence shows that I is a rapidly converging Fourier

series, and that the frequency of the fundamental is the same as the frequency of the input e.m.f. on the grid.

We can therefore write:

$$I = a_0/2 + \sum_{n=1}^{\infty} \alpha_n \sin npt + \sum_{n=1}^{\infty} \beta_n \cos npt \tag{11}$$

In terms of the exponential values for the sine and cosine,

$$2\alpha_n \sin npt + 2\beta_n \cos npt = (\beta_n - i\alpha_n)\, e^{\,inpt} + (\beta_n + i\alpha_n)\, e^{\,-\,inpt}.$$

Write

$$2a_n = \beta_n - i\alpha_n, \qquad \text{and} \qquad 2b_n = \beta_n + i\alpha_n. \tag{12}$$

Then

$$I = a_0/2 + \sum_{n=1}^{\infty} a_n\, e^{\,inpt} + \sum_{n=1}^{\infty} b_n\, e^{\,inpt}. \tag{13}$$

If we substitute this value of I in equation (10), we can arrange the resulting terms in ascending orders of e^{ipt} and in descending orders of e^{ipt}. The expression will not be given here as it is very lengthy and cumbersome. Since we have terms involving e^{ipt} and e^{ipt} and corresponding higher powers of e on both sides of the equation, the coefficients of the like powers on either side may be equated. Hence we obtain a series of $2n$ equations from which the a's and b's can theoretically be determined. The general solution of these equations, while ideally possible, is impracticable without further assumptions as to the nature of the coefficients. We saw in the case of the resistance of the plate circuit, that only the first few terms of the series were of importance for values of e within the limits of equation (2), and that for values of e up to 10 or 15 volts, the amplitude of the fundamental varied approximately as the first power of e. If all the coefficients other than a_0, a_1, and b_1, are negligible, we have:

$$a_1 = \frac{BA^{1/2}\mu e}{1 + 2BLip}, \qquad b_1 = \frac{BA^{1/2}\mu e}{1 - 2BLip}, \tag{14}$$

showing that, for this case, a_1 and b_1 are linear functions of e. Substituting the above values of a_1 and b_1 in the expressions for a_2 and b_2, we have:

$$\begin{aligned} a_2 &= \frac{A\mu^2 e^2}{4\,(1 + 2\,BLip)^2\,(1 + 4\,BLip)}; \\ b_2 &= \frac{A\mu^2 e^2}{4\,(1 - 2\,BLip)^2\,(1 - 4\,BLip)}. \end{aligned} \tag{15}$$

The values of a_2 and b_2 were found on the assumption that all the higher coefficients were negligible. Similarly a_3 and b_3 may be found and so on.

From relation (22) the values of α_1, β_1, α_2, β_2, etc., may be found, and

$$\alpha_1 \sin pt + \beta_1, \cos pt = \frac{\mu\, e \cos (pt - \alpha)}{(R_0 + l^2p^2)^{1/2}}, \text{ where } \alpha = \tan^{-1}\frac{lp}{R_0} \tag{16}$$

$$\text{and } R_0 = \frac{1}{2\,A\,(E_b + \mu E_c + \epsilon)},$$

$$\alpha_2 \sin 2\,pt + \beta_2 \cos 2\,pt = \frac{A\mu^2e^2 \cos (2\,pt - \beta)}{2\,(R_0^2 + l^2p^2)\,(R_0^2 + 4\,l^2p^2)^{1/2}}, \tag{17}$$

where

$$\beta = \tan^{-1}\frac{2lp}{R_0}\left[\frac{2\,R_0^2 - l^2p^2}{R_0^2 - 5\,l^2p^2}\right].$$

Similarly $\alpha_3 \sin 3\,pt + \beta_3 \cos 3\,pt$ may be found and so on for the higher terms.

Since $I = a_0/2 + \Sigma\alpha_n \sin (npt) + \Sigma\beta n \cos npt$, the addition of the various quantities found above will give the resulting current I.

It is obvious that as soon as the values of a_2 and b_2 become appreciable compared with a_1 and b_1, the values of the latter obtained above can no longer be correct, since they were determined on the basis that all the other coefficients were negligible.

If the values obtained for a_2 and b_2 are substituted in the equations for a_1 and b_1, the following is the value of

$$\alpha_1 \sin pt + \beta_1 \cos pt = \frac{\mu e \cos (pt\,(pt - \alpha)}{(R_0^2 + l^2p^2)^{1/2}}$$

$$+ \frac{2\,R_0^5\,A^2\mu^3e^3\,lp \cos (pt - \epsilon)}{(R_0^2 + l^2\,p^2)^2\,(R_0^2 + 4\,l^2p^2)^{1/2}}, \tag{18}$$

where

$$\alpha = tan^{-1}\frac{lp}{R_0}\,\epsilon = tan^{-1}\frac{R_0}{2\,lp} \text{ and } \left(\frac{l^2p^2 - 2\,R_0^2}{R_0^2 - 5\,l^2p^2}\right).$$

In order to obtain a numerical value for $\alpha_1 \sin (pt) + \beta_1 \cos pt$, it is best to evaluate each term separately and then compound the results by the parallelogram law. Similarly if the values of a_3 and b_3 become comparable with a_2 and b_2, we find for the corrected value of

$$\alpha_2 \sin 2\,pt + \beta_2 \cos 2\,pt = \frac{R_0^3\,A\mu^2e^2 \cos (2\,pt - \beta)}{2\,(R_0^2 + l^2p^2)\,(R_0^2 + 4l^2p^2)^{1/2}}$$

$$+ \frac{12\,R_0^7\,A^3\,\mu^4e^4\,l_2p_2 \cos (2\,pt - \lambda)}{(R_0^2 + l^2p^2)^2\,(R_0^2 + 4\,l^2p^2)\,(R_0^2 + 9l^2p^2)^{1/2}}$$

where β is the same as defined in (27) and

$$\lambda = \tan^{-1}\frac{3lp}{R_0}\left(\frac{3\,R_0^4 - 17\,l^2p^2R_0^2 - 8\,l^4p^4}{R_0^4 - 32\,l^2p^2\,R_0^2 + 40\,l^4p^4}\right).$$

By making successive approximations as many terms as desired may be included in the expressions for any particular harmonic. It will be noticed that the resulting angle of lag of each harmonic depends on the number of terms we include in the coefficient, and thus there arises a peculiarity in a vacuum-tube generator, namely that the angles of lag of the various output harmonics are dependent on the amplitude of the input wave on the grid. The larger the amplitude for the coefficients of the various harmonics, and the consequent shifting of the angles of lag results.

Area of the Characteristic Loop.

Since the fundamental plate current lags behind the grid voltage by an angle $\alpha = \tan^{-1}(lp/R)$, it is evident that if this current be plotted against the alternating grid voltage an elliptical characteristic will be produced. If, however, the first and higher harmonics are plotted in addition to the fundamental, and the curves thus formed compounded into a single curve, it is evident that the characteristic will no longer be a true ellipse. Since the amplitudes of the harmonics are small compared to that of the fundamental, the resulting curve will not seriously depart from an ellipse. This curve is what is usually referred to as the dynamic characteristic. The $a_0/2$ term of the series gives the point of operation on the static characteristic, and it is obvious from the expression for the latter, that the larger the harmonics become, the greater is the shift of this point of operation. In practice this shift is noticed by the increased reading of a direct-current milliameter.

If all but the fundamental current is omitted, the area of the loop may be easily found.

Put $x = E_c + e\cos(pt)$

$$y = \frac{1}{2}a_0 + \frac{\mu e}{(R_0^2 + l^2p^2)^{1/2}}\cos(pt - \alpha)$$

Limits for pt are o and 2π

$$\text{Area} = \int_0^{2\pi} y dx = -\int_0^{2\pi}\left\{ ao/2 + \frac{\mu e}{(R_0^2 + l^2p^2)^{1/2}}\cos(pt - \alpha)\right\}\sin pt\, dt$$

$$= \frac{2\pi e^2 u \sin\alpha}{(R_0^2 + l^2p^2)^{1/2}} = \frac{2\pi \mu e^2 lp}{(R_0^2 + l^2p^2)}, \text{ since } \alpha = \tan^{-1}\frac{lp}{R_0}.$$

If the curve be referred to the I_b, E_b axes, this expression must be multiplied by μ. Also since the maximum value I_0 of the fundamental is $\mu e(R_0^2 + l^2p^2)^{-1/2}$, the area of the loop may be written as

$$A = 2\pi I_0^2 lp = 2\pi \frac{lp}{R_0} R_0 I_0^2.$$

Since $lI_0^2/2$ = the maximum dynamical energy in the inductance, the area of the loop is thus proportional to that quantity. If the inductance were not present $A = 0$, which means that the characteristic no longer has the form of a loop, but reverts back to the type found when a resistance was placed in the plate circuit.

Case of a Capacity in the Plate Circuit.

Since a condenser placed between the plate and the battery prevents the direct current from flowing, it is necessary to place a choke coil across the condenser. The choke coil will allow the direct current to pass, but if made properly will offer almost an infinite resistance to the high-frequency current.

The solution for this case is directly analogous to that for the inductance problem, the only difference in the final result being that $1/cp$ always replaces lp.

Thus the simple expression for the fundamental becomes $\mu e/(R_0^2 + 1/c^2p^2)^{1/2} \cos(pt + \alpha)$ where $\alpha_1 = \tan^{-1} 1/R_0cp$. Similar expressions for the other harmonics may be found from comparison with the expressions found for the inductance.

The dynamic characteristic for this case is similar to that found for the inductance, the only difference being that it is traced out in the opposite direction.

Description of Apparatus and Experimental Procedure.

In order to have an experimental set-up which could be used to verify the preceding theory, the following conditions and requirements had to be met.

(*a*) Production of a pure sine wave e.m.f.

(*b*) Use of a sufficiently low frequency that capacity effects might be of small magnitude.

(*c*) Accurate measurement of the input e.m.f. on the grid of the harmonic producing tube.

(*d*) Use of a pure resistance.

(*e*) Use of a pure inductance.

(*f*) Measurement of the amplitude of the harmonics produced, without introducing extraneous resistances, etc., into the harmonic producer.

Fig. 1 is the complete circuit diagram of the entire collection of apparatus used in the experimental work. It may be divided into three main sections, the oscillator, harmonic producer and the harmonic analyzer. The oscillator in the upper left corner is designed so as to produce as pure a sine wave as possible. The tuned circuit L^1C^1 prevents

the fundamental frequency from passing into the battery circuit, thus compelling it to travel to the filament through the inductance L_3 of the oscillating circuit. The condenser C_1 offers less and less impedance to

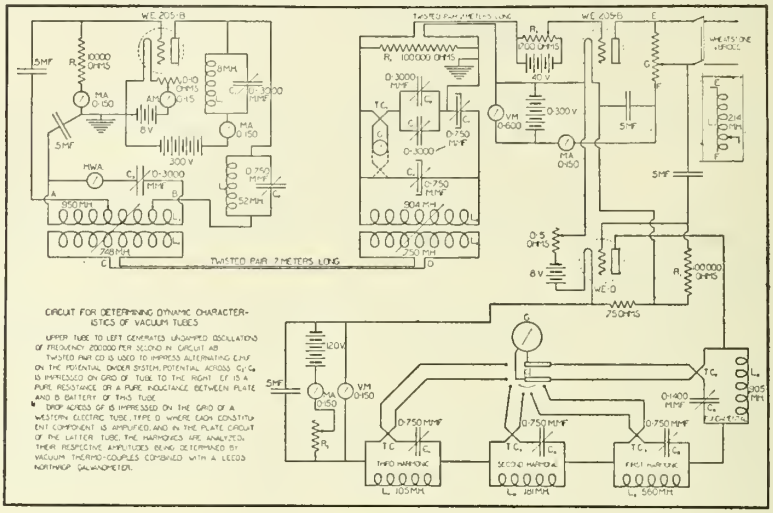

Fig. 1.

the higher harmonics, and the latter will pass down through C_1 to the filament terminal. As the first harmonic is always appreciable, it was specially filtered out of the oscillating circuit L_3C_3, by means of the anti-resonant circuit L_2C_2. The inductance L_2 = .52 M.H., of course offered some impedance to the fundamental frequency, but that was negligble compared with the impedance that L_1C_1 offered to the fundamental. These filters thus helped to produce a pure sine-wave oscillation of the same frequency as the fundamental in the circuit L_3C_3. The frequency used throughout was 200,000 cycles per sec., or a wave-length of 1,500 meters. This frequency was high enough that it could be tuned very sharply, and yet not so high that the internal capacities of the tubes would be of any importance. Ballantine[1] has worked out expressions for the input impedence of tubes under various conditions, and applying his formulæ to the W. E. 205 *B* tube at this frequency and under the experimental conditions which will be described below, the input impedance was found of the order of 100,000 ohms.

The inductance L_4 was loosely coupled to L_3 and connected by means of a twisted pair with L_5, which in turn was loosely coupled to L_6. These latter coils were placed about seven meters away from the oscillating circuit, in order that they might not pick up any of the harmonics. The

[1] PHYS. REV., 15, p. 409–420, 1920.

loosening of the couplers already described resulted in maintenance of the sine e.m.f. The combination of condensers C_4, C_5, C_6 and C_7 and the inductance L_6 is tuned for the fundamental frequency. The arrangement of these condensers is what is known as a potential divider and has been described by Hulbert and Breit.[1] The object is to take a portion of the alternating e.m.f. across L_6 and impress it on the grid of a tube. When the thermocouple is in the dotted position the current passing through C_4 is measured, but the current passing through C_5 and C_6 can easily be calculated when the values of the different capacities are known. The object of measuring the current in C_4 is that for small values of input potentials, the currents passing through C_5 and C_6 would be too small to be recorded by a low resistance thermo-couple. If I represents the amplitude of the alternating current passing through C_5 and C_6 then the resulting input e.m.f. is $1/2\ \pi\ (C_5 + C_6)\ f$, where f is the frequency of the wave. For an e.m.f. of over one volt, the current I could be measured directly by the low resistance thermo-couple.

The resistance R_2 is used to provide a leak for any charge that may accumulate on the grid, and allow it to flow to earth. Its resistance must be comparable to the input impedance of the tube. By means of potentiometer R_3 the potential on the grid could be varied as desired.

The upper tube to the right is the harmonic producer. By means of the condenser potential divider a known value of input e.m.f. was impressed between the grid and filament and then according to equations (4), for a resistance EF in the plate circuit, and (9) for an inductance EF, a plate current will result which is capable of being represented as a series of harmonics. In order to get the results predicted in equation (4), EF must be a pure resistance. A straight wire immediately suggests itself as a resistance which would possess a minimum inductance and capacity. However, in order to obtain a resistance of the order of 3,000 ohms, so much wire would be needed, that inductive and capacitive effects would become appreciable. Then again, it is a well-known fact the conductivity of a wire diminishes with the frequency owing to the skin effect, and consequently the exact value of the resistance at any particular frequency is not easily determined. A resistance suitable for high-frequency work should have a negligible skin effect, as well as having negligible inductance and capacity. On the suggestion of Professor W. F. G. Swann, the author tried out some platinized quartz fibers immersed in acid-free paraffin oil, and found that they would carry currents up to at least 60 milliamperes. From the formula for change in resistance with frequency,[2] it can be shown that using fibers about .01 mm.

[1] Phys. Rev., 4, p. 278, 1920.

[2] J. A. Fleming, Wireless Telegraphy, p. 97.

in diameter, the skin effect can be neglected. As the fibers used had a resistance of about 100 ohms per cm. only a short length of circuit was needed, thus reducing the inductance and capacity. The inductance EF was wound with No. 16, D.C.C. copper wire, and the windings were spaced about 1 mm. apart. The resistance of the coil was 10 ohms, whereas the reactance was 2,700 ohms.

In order to detect the various harmonics, a fraction of the e.m.f. along EF was impressed on the grid of a W. E. Co. V tube, this impressed e.m.f. being always less than 1 volt. A 100-ohm slide wire of IAIA wire was used for the variable portion of EF. It can be seen from equation (8) that in order to obtain pure amplification without the introduction of harmonics whose amplitudes are appreciable compared to that of the fundamental, the input e.m.f. must be small (less than one volt), and the value of the external resistance must be high. The resistance of an anti-resonant circuit is $R + (L^2\omega^2)/R$, where $L\omega$ is the inductive reactance. Since R, the ohmic resistance, is negligble, at radio frequencies, in comparison with $(L^2\omega^2)/R$, the latter term may be taken as the value of the resistance of an anti-resonant circuit. Therefore for any given ω, L should be made as large, and R as small as possible. Now in the plate circuit of the tube which is used to separate out the harmonics, a series of anti-resonant circuits are placed. The first one is tuned for the fundamental, the second for the first harmonic, and so on. A vacuum thermocouple is placed in each circuit on the capacity side. This is done so that the D.C. plate current will not affect it. In order to keep the ohmic resistance low, thermocouples with heater resistances of from 0.5 ohm to 5 ohms were used, the higher resistance thermo-couples being used to measure the weaker amplitudes of the higher harmonics.

The effective resistance of these circuits are as follows: fundamental, 120,000 ohms; first harmonic, 183,000 ohms; second harmonic, 95,000 ohms; third harmonic, 175,000 ohms.

Arrangements (not shown in Fig. 1) were also made for measuring higher harmonics than these, by changing the inductance L_{11}, and by retuning C_{11}. Each thermo-couple could be connected successively to a Leeds and Northrup galvanometer, and the deflection of the latter indicated the root-mean square value of the alternating current passing through the heater. Previous to placing the thermo-couples in the circuits, they were calibrated using alternating current (60 cycles). It will be seen that the harmonic analyzer is essentially a voltage amplifier, picking out each frequency in the producer and magnifying its voltage. For this reason a tube with a large voltage amplification constant was chosen, in fact the value of μ as given by equation (4) was 26.

Let I_1 = the maximum current in the fundamental circuit.
Let R_1 = the effective resistance.
Let R_0 = the internal output resistance of the V tube.

Therefore $R_1 I_1$ = e.m.f. across L_8.
Let e = e.m.f. across FG.
Let μ^1 = actual voltage amplification factor.

$$\text{Therefore } \mu^1 = \frac{\mu R_1}{R_0 + R_1} = \frac{26 \times 120{,}000}{29{,}250 + 120{,}000} = 20.8.$$

$$\text{Therefore } e = \frac{R_1 I_1}{20.8} = \frac{120{,}000 \times I_1}{20.8}$$

Let r = resistance of FG.
Let i = amplitude of current of fundamental frequency passing through FG.

$$\text{Therefore } ri = e \text{ and } i = \frac{120{,}000.\ I_1}{20.8 \times r}. \qquad (15)$$

Thus knowing I_1 from the galvanometer deflection, and r from the Wheatstone Bridge, the value of i can be determined. For the case worked out above i represents the amplitude of the fundamental frequency produced by a pure sine wave impressed on the grid of a tube having a pure resistance load in the plate circuit. Similarly, by measuring the currents in the other tuned circuits we can work back to the equivalent current in the harmonic producer.

When the resistance EF is replaced by an inductance, a portion FG of the inductance is used to obtain the input on the grid of the analyzer. In this case it will be noted that EF offers twice as much impedance to the first harmonic, three times as much to the second harmonic, and so on. This makes it possible to measure weaker harmonics than in the case of the resistance. The inductance of GF in this experiment was 0.0587 milli-henry, whereas the whole inductance of EF was 2.14 milli-henries. The input impedance of the analyzer to which EF was attached was of the order of 50,000 ohms at 200,000 cycles per sec., whereas the impedance of .0587 henry is only 74 ohms. This showst hat the impedance of the analyzer was practically short-circuited by the coil FG, and consequently did not affect the nature of the external circuit of the producer. For measurement of large output current values, the value of FG was reduced to 0.04 M.H. To obtain, say the amplitude of the fundament current with the inductance, we have an equation

analogous to (15),

$$i = \frac{120{,}000\, I}{20.8\,(l\omega)},$$

where l is the inductance of FG and $\omega = 2\,\pi \times$ the frequency.

Experimental Results.

The following constants for the 205-B tube were determined from its static characteristic. $A = .554 \times 10^{-6}$, $\epsilon = 7.5$ volts, $\mu = 6.7$. For $E_b = 260$ volts, $E_c = -7.5$ volts, $R_0 = 1/2\,A\,(E_b + \mu\,E_c + \epsilon) = 3{,}570$ ohms.

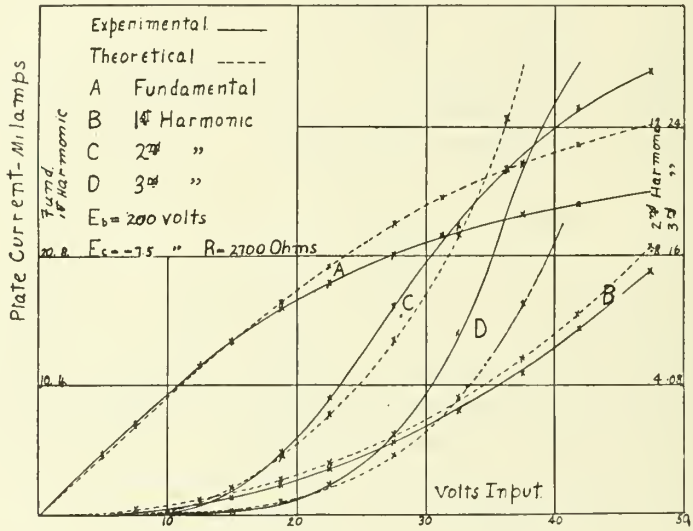

Fig. 2

Resistance in Plate Circuit.—When a resistance of 2,700 ohms was placed in series with the plate, and the value of E_b reduced to 200 volts, the plate current was 21.5 milliamperes. Using these values of potential and resistance the curves shown in Fig. 2 were obtained. The amplitude of the input e.m.f. was varied from 0 up to 50 volts. The latter maximum loaded the tube rather heavily, and the larger currents were maintained just long enough to obtain the necessary readings.

Keeping the e.m.f. of the input at 15 volts, the actual plate potential at 200 volts, and varying the static grid potential the curves in Fig. 3 were obtained, for ranges of E_c between $-$ 30 and $+$ 12 volts.

With a static voltage of $-$ 7.5 on the grid and the alternating e.m.f. kept at 15 volts, the variation of the harmonics with plate voltage was determined, as in Fig. 4.

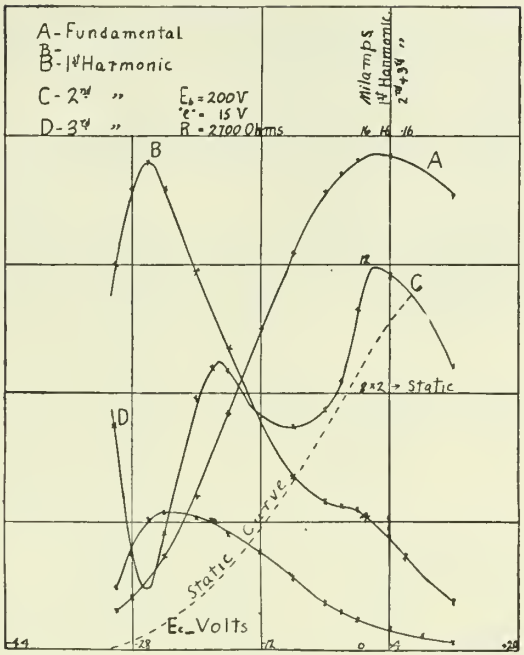
A-Fundamental
B-1st Harmonic
C-2nd "
D-3rd "
Eb = 200V
"e" = 15 V
R = 2700 Ohms
Milamps
1st Harmonic
2nd + 3rd "
A
B
C
D
8×2 → Static
Static Curve
Ec_Volts

Fig. 3

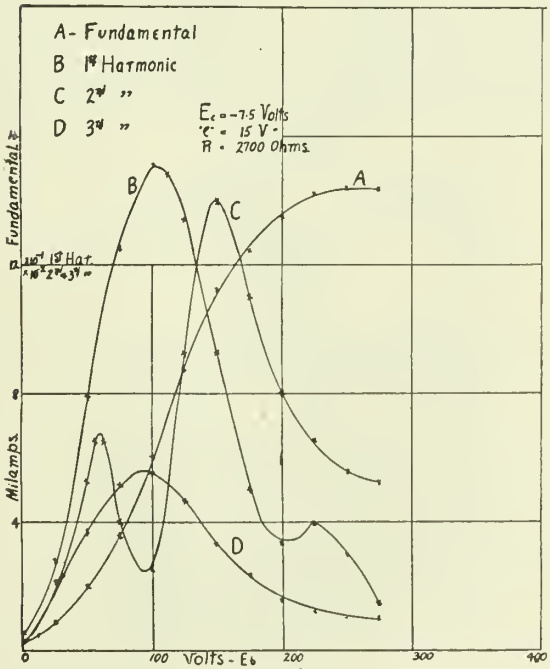
A- Fundamental
B 1st Harmonic
C 2nd "
D 3rd "
Ec = -7.5 Volts
"e" = 15 V
R = 2700 Ohms
Fundamental
Milamps
A
B
C
D
0
100
Volts - Eb
200
300
400

Fig 4

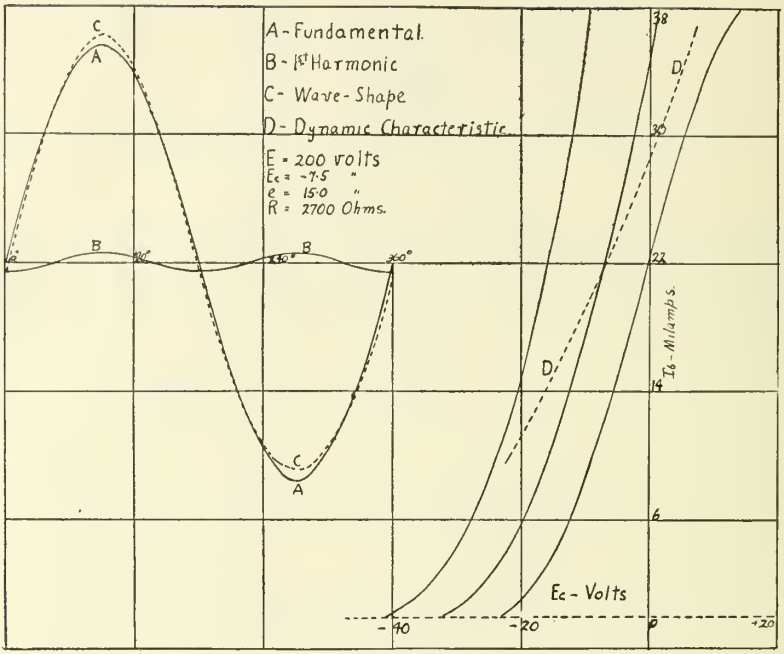

Fig-5

Fig. 5 represents the wave-shape of the plate current obtained when a pure sine wave e.m.f. of 15 volts is impressed on the grid, the plate and grid potentials being the same as stated above. The fundamental and first harmonic are the only components included in the wave-shape. The

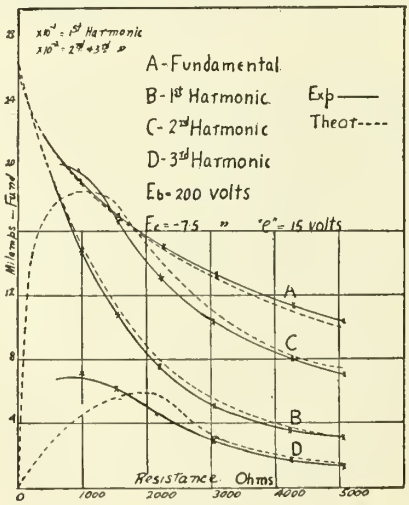

Fig. 6

amplitudes of the other harmonics are too small to be shown on the same scale. Fig. 5 also shows the dynamic characteristic for this case, where the wave-shape thus obtained is plotted against the alternating input voltage.

In Fig. 6 the variation of the harmonics with the value of the external resistance is shown.

Inductance in Plate Circuit.—Exactly similar experimental procedure was undertaken for the inductances. A higher plate voltage and plate current was used here, since there were no delicate platinized quartz fibers to be dealt with. For this case

$$E_b = 250 \text{ volts}, E_c = -10 \text{ volts}, R_0 = \frac{1}{2A\ (E_b + \mu E_c + \epsilon)} = 3{,}800 \text{ ohms}$$

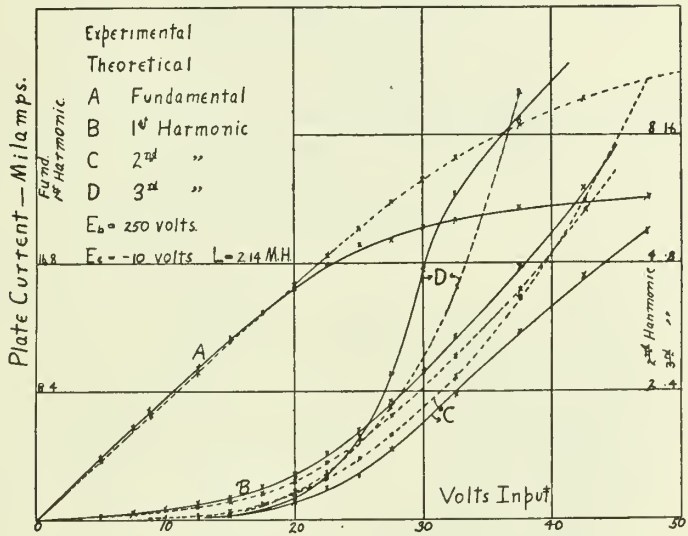

Fig. 7

The reactive load in the plate circuit was 2,700 ohms. Fig. 7 shows the variation of the harmonics with the alternating e.m.f. on the grid, under the conditions given above.

In Fig. 8 is shown the variation of the harmonics with the value of the static grid potential, the alternating input e.m.f. being constant at 20 volts, and the plate voltage being 250 volts. Fig. 9 shows how the variation of the static plate voltage affects the values of the harmonics.

The curves of Fig. 10 give the variation of the harmonics with the magnitude of the inductance in the plate circuit.

Fig. 11 represents the wave shape, using only the values of the fundamental and first harmonic.

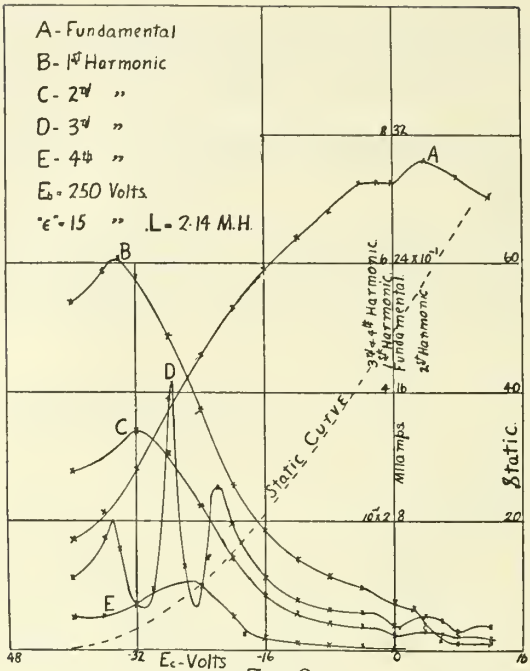
A - Fundamental
B - 1st Harmonic
C - 2nd "
D - 3rd "
E - 4th "
Eb = 250 Volts
"ε" = 15 " L = 2.14 M.H.
Static Curve
3rd & 4th Harmonic
1st Harmonic
Fundamental
2nd Harmonic
Milamps
Static
Ec - Volts
48
32
16
0
16
8
32
6
24 x 10⁻¹
60
4
16
40
10⁻¹ x 2
8
20

Fig. 8

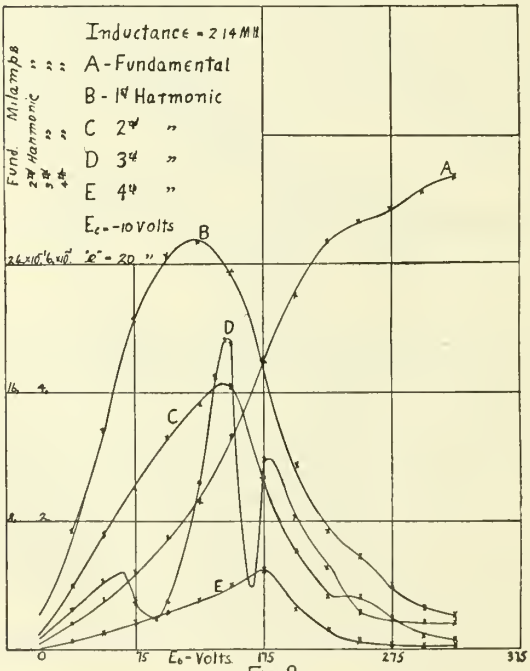
Inductance = 2.14 MH
A - Fundamental
B - 1st Harmonic
C 2nd "
D 3rd "
E 4th "
Ec = -10 Volts
"ε" = 20 "
Fund. Milamps
2nd Harmonic
3rd
4th
Eb - Volts
0
75
175
275
375
16
4
8
2

Fig. 9

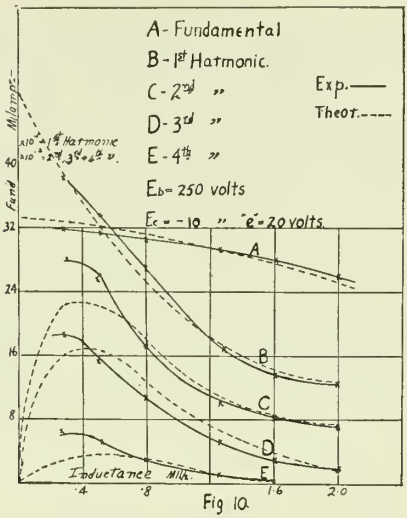

Fig 10.

Fig. 11 also represents the dynamic characteristics for this case, the area of this loop being proportional to the amount of energy delivered.

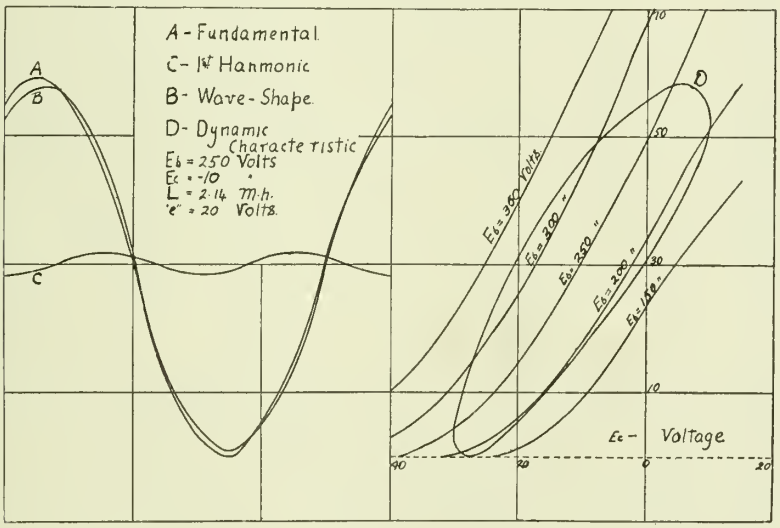

Fig. 11.

Discussion of Results.

The theoretical curves as shown in the various figures, are plotted from the values of the coefficients given by equations (3) and (8). In the case of the resistance the experimental fundamental values check up very closely with the theoretical values up to an input voltage of fifteen volts.

Beyond that voltage equation (3) no longer accurately represents conditions. It will be noticed that the maximum positive potential to which the grid is raised in this operation is 7.5 volts. Fig. 5 shows that at this voltage the static characteristic begins to flatten out, due to the passage of electrons to the grid instead of to the plate. For voltages higher than fifteen the theoretical first and third harmonics fall below the experimental values, whereas the second harmonic is greater than the experimental values would indicate. This would seem to be due to the flattening out of the wave at the upper end of the characteristic. In the case of the inductance good agreement between theoretical and experimental values were found for input voltages as high as 20 volts. This is due to the fact in this case that the operation was carried out over the 250-volt static characteristic, and it will be seen from Fig. 11 that this curve does not begin to flatten out until a positive grid voltage of ten volts is reached. This point of operation coincides with the maximum positive voltage to which the grid was raised with an input e.m.f. of 20 volts, E_c being $-$ 10 volts.

The curves of Figs. 3 and 8 show, in an emphatic manner, that the further we move towards the straighter portion of the static characteristic, the greater the fundamental becomes while the other harmonics continue to diminish. At $-$ 40 volts the higher harmonics were still very much in evidence although the fundamental was rapidly approaching zero. The second harmonic in the resistance curves and the third in the inductance curves show rather peculiar irregularities. The sharp maxima and minima would at first seem to point to some sort of internal resonance in the tube. It will be noticed, however, that these are produced by simply varying either the grid or plate potentials, and are probably due to irregularities in the static characteristic which are smoothed out in the ordinary process of plotting. It will be recalled that in the case of the resistance the coefficient of the second harmonic is principally determined by the value of the third derivative of the current function. A small unnoticeable irregularity in the static characteristic might produce a large variation in the third derivative, and this effect is magnified by this method of analysis. In the case of the inductance the coefficients cannot be expressed as simple derivatives, but some such explanation as that given above will probably hold good here also.

The curves of Figs. 4 and 9 show that the greater the plate potential the greater the fundamental becomes while the harmonics continue to diminish. Beyond a certain plate potential, about 300 volts, the fundamental becomes nearly constant in value. The curves which exhibited the irregularities in the grid-variation series, also exhibit similar irregu-

larities here. Further they occur at the same value of $(E_b + \mu E_c)$ showing that the effect is independent of whether the grid or plate potential is increased provided the sum as given is the same.

The curves of Figs. 6 and 10 show how the harmonics depend on the external impedance. Using this method of analysis it was impossible to use an impedance much less than 500 ohms. Even at this value, the input impedance of the analyzing tube cannot be neglected. Hence, beyond the first harmonic the experimental and theoretical curves do not agree very closely in this region. Although the experimental curves show signs of flattening out at this low impedance, they should have been rapidly approaching zero. For zero resistance or inductance, the fundamental and first harmonic have the values given by equation (2a), and all the other harmonics are zero, which is also in accordance with the same equation.

If all the harmonics were neglected the wave-shape for the resistance would be a pure sine wave in phase with the impressed e.m.f. These two, when compounded, would give a straight-line dynamic characteristic. It may be seen that with a sufficiently high resistance in the plate circuit this condition may be nearly reached. However, if the higher harmonic were also taken into consideration, the dynamic characteristic would be no longer linear but would have a curvature, which would be much less than that of the static curve. With the inductance, if all but the fundamental had been neglected the current would have been a pure sine wave lagging behind the impressed e.m.f. by an angle $\theta = \tan^{-1} lp/R$. The dynamic characteristic under those conditions would have been an ellipse. Addition of the other harmonic components tends to flatten out the sine wave, and consequently distort the purely elliptical characteristic.

In calculating the theoretical values of the coefficients of the various harmonics, up to a range of 15 or 20 volts, the coefficients of the fundamental were practically proportional to the first power of the applied e.m.f.; the first harmonic was proportional to the second power; and so on. It was only for values of the input voltage beyond 20 volts that the more complicated expressions for the coefficients had to be evaluated.

In conclusion, the writer wishes to express his very sincere thanks to the Western Electric Company, Inc., of New York, for their kindness in loaning necessary tubes and vacuum thermo-couples, and also to Professor W. F. G. Swann of this department for his many helpful suggestions and criticisms and his invaluable encouragement at all times.

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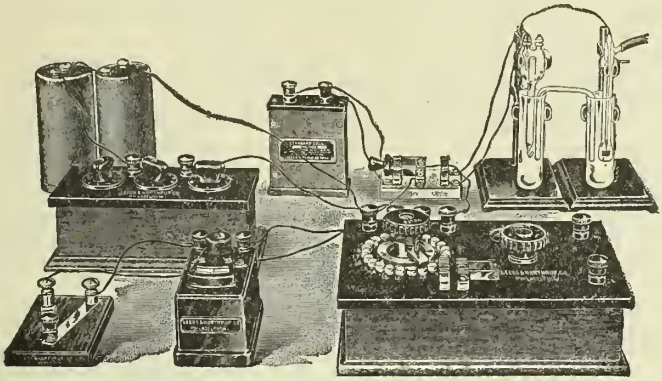

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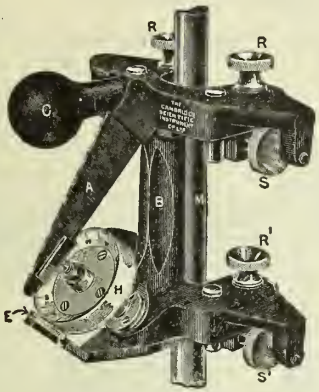

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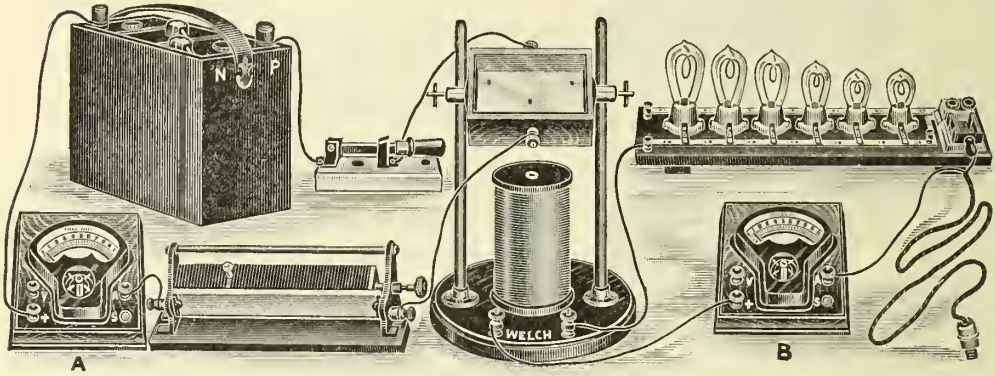

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1. *Material not new* need not be analyzed or described; a valuable summary of previous work, however, should be noted.

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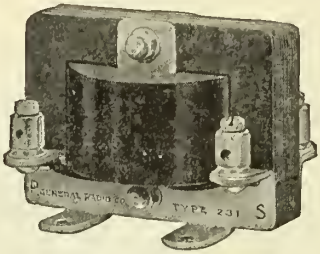

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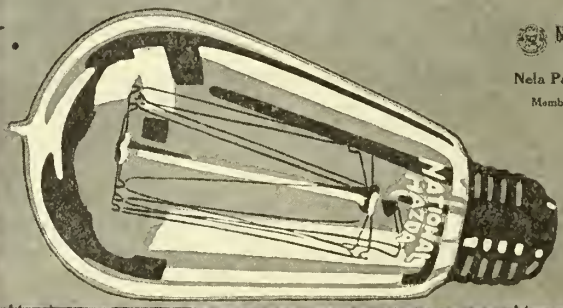

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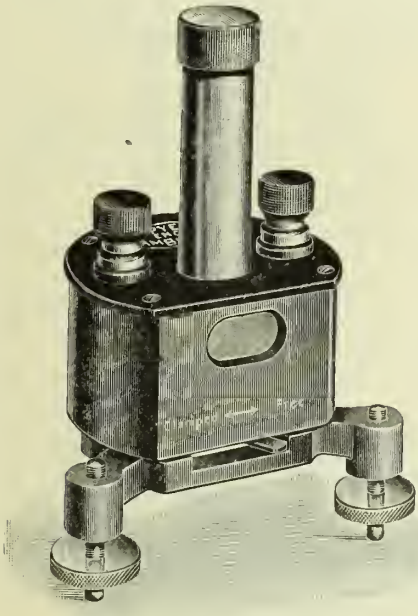

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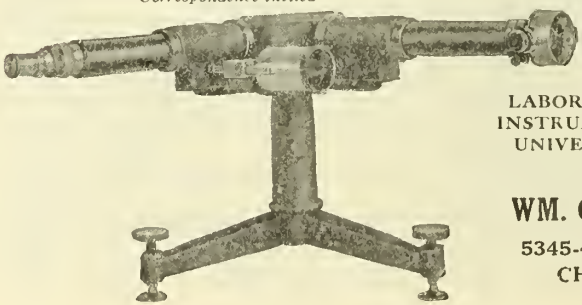

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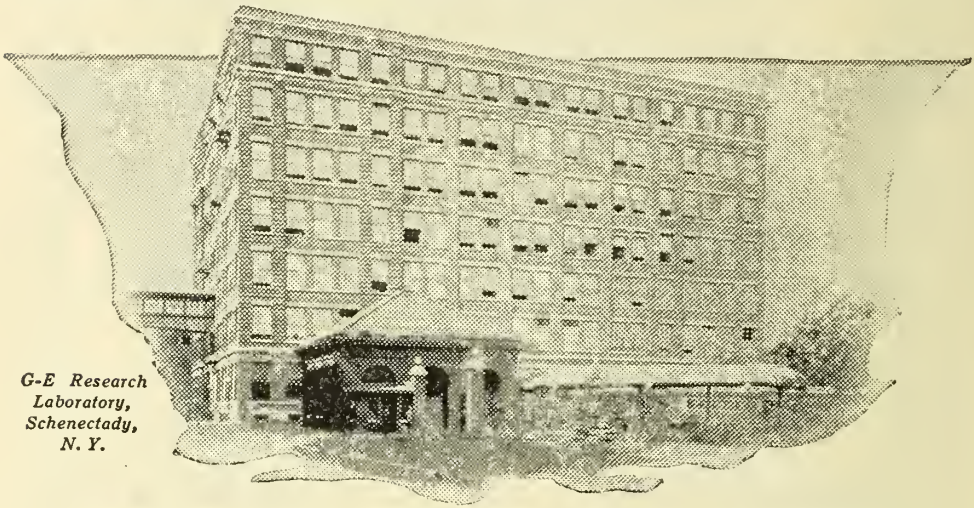

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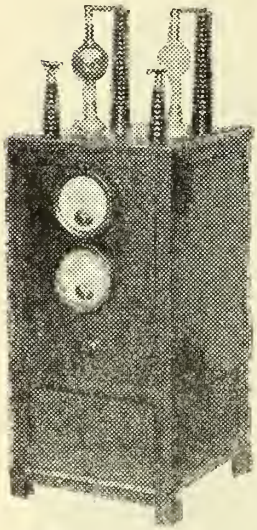

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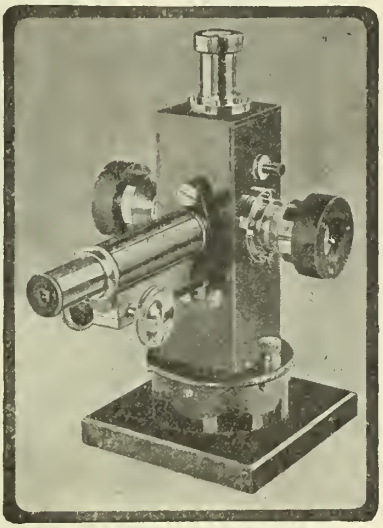

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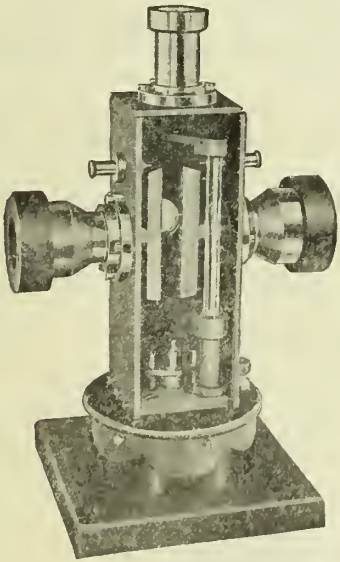

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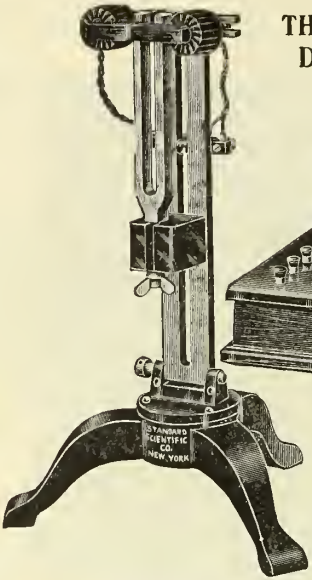

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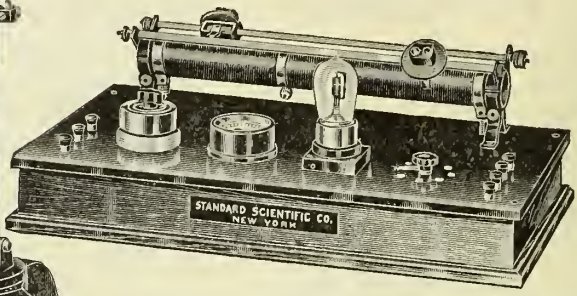

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